Supplementary Information

Isomorphous Series of Pd^{II}-Containing Halogen-Bond Donors Exhibiting Cl/Br/I Triple Halogen Isostructural Exchange

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S1. Materials and instrumentation

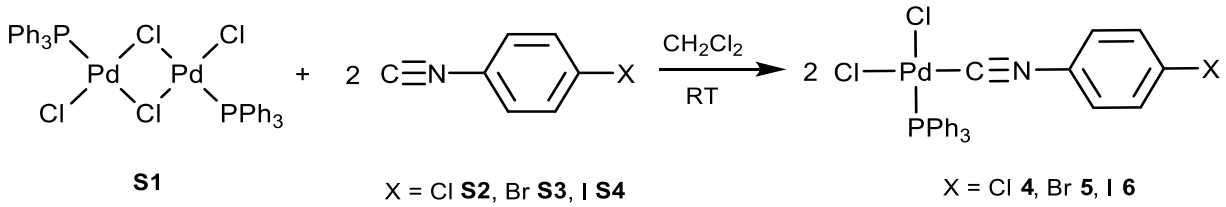
Reagents and materials used. Solvents, $PdCl_2$, formic acid and anilines were obtained from commercial sources and used as received. Complex $[PdCl_2(PPh_3)]_2$ [1] and isocyanides [2] were synthesized by the literature procedures. Complexes *trans*-$[PdI_2(CNC_6H_4X)_2]$ (X= Cl, Br; I) were prepared as reported earlier [2].

Instrumentation and methods. Mass-spectra were acquired on Bruker micrOTOF spectrometer equipped with ESI source; a CH_2Cl_2/MeOH mixture was used as the solvent. The instrument was operated at positive ion mode using *m/z* range of 50–3000. The capillary voltage of the ion source was set at –4500 V (ESI^+) and the capillary exit at +(70–150) V. The nebulizer gas pressure was 0.4 bar and drying gas flow was 4.0 L/min. The most intensive peak in the isotopic pattern is reported. Infrared spectra were recorded on Bruker Tensor 27 FTIR instrument (4000–200 cm^{-1}, resolution 2 cm^{-1}) in KBr pellets. ^1H, $^{13}C\{^1H\}$ NMR spectra, and ^1H, ^{13}C-HMQC/HSQC and ^1H,^{13}C-HMBC NMR correlation experiments were acquired on a Bruker Avance 400 spectrometer. NMR spectra were acquired in $CDCl_3$ at 20 °C. Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated solvent ($CHCl_3$: δ 7.26 (^1H), 77.20 (^{13}C)).

X-ray Structure Determinations. Single-crystal X-ray diffraction experiment carried out using Agilent Xcalibur diffractometers with monochromated MoKα radiation. The crystal was fixed on a micro mount, placed on a diffractometer, and measured at 100(2) K. The unit cell parameters were refined by least-squares techniques in the 2θ range of 6.0–55.0 for MoKα. Structures have been solved by the Superflip [3, 4] structure solution program using Charge Flipping and refined by means of the ShelXL [5] program incorporated in the OLEX2 program package.[6] Empirical absorption correction was applied in CrysAlisPro (Agilent Technologies, 2012) program complex using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. Crystallographic details are summarized in **Tables S1**, **S2**.

S2. Synthetic work and characterization

Synthesis of *cis*-[$PdCl_2$(CNR)(PPh_3)] (4–6). A solution of an isocyanide CNC_6H_4-4-X (X = Cl, Br, I; 0.10 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a suspension of [$Pd_2Cl_4(PPh_3)_2$] (;46 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) at RT. The resulting bright yellow solution was filtered off to remove some insoluble material, the filtrate was then evaporated at 20–25 °C in vacuum to dryness to give **5**–**7** as yellow solids. These species are well soluble in dichloromethane, chloroform, and sparingly soluble in diethyl ether.



S1 X = Cl **S2**, Br **S3**, I **S4** X = Cl **4**, Br **5**, I **6**

Scheme S1. Synthesis of **4**–**6**.

***cis*-[$PdCl_2$(CNC_6H_4-4-Cl)(PPh_3)] (4).** Yield 55 mg (95%). HRESI$^+$-MS (*m/z*): calc. for $C_{26}H_{23}Cl_2NOPPd$ 573.9926, found 573.9919 $[M - Cl + CH_3OH]^+$. IR (KBr, selected bands, cm^{-1}): ν(C–H) 3038 (m), 2974 (m), 2924 (m); ν(C≡N) 2209 (s). ^1H NMR ($CDCl_3$, *δ*): 6.86 (d, 2H, *o*-H from CNR, *J* = 8.70 Hz), 7.30 (d, 2H, *m*-H from CNR, *J* = 8.70 Hz), 7.43–7.50 (m, 6H, *m*-H from PPh_3), 7.51–7.58 (m, 3H, *p*-H from PPh_3), 7.75–7.84 (m, 6H, *o*-H from PPh_3). $^{13}C\{^1H,^{31}P\}$ NMR ($CDCl_3$, *δ*): 127.71 (*o*-CH from CNR), 128.87 (*m*-CH from PPh_3), 129.30 (*ipso*-C from PPh_3), 129.84 (*m*-CH from CNR), 131.88 (*p*-CH from PPh_3), 134.46 (*o*-CH from PPh_3) 137.38 (*p*-C–Cl from CNR); the signals of isocyanide carbon atom C^0 and the carbon atom C^1 adjacent to the isocyanide group were note detected. $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): 27.77.

***cis*-[$PdCl_2$(CNC_6H_4-4-Br)(PPh_3)] (5).** Yield 57 mg (92%). HRESI$^+$-MS (*m/z*): calc. for $C_{26}H_{23}BrClNOPPd^+$ 617.9401, found 617.9426 $[M - Cl + CH_3OH]^+$. IR (KBr, selected bands, cm^{-1}): ν(C–H) 3084 (m), 3056 (m), 3022 (m); ν(C≡N) 2221 (s). ^1H NMR ($CDCl_3$, *δ*): 6.79 (d, 2H, *o*-H from CNR, *J* = 8.5 Hz), 7.43–7.50 (8H, {2H, *m*-H from CNR} + {6H, *m*-H from PPh_3}), 7.50–7.56 (m, 3H, *p*-H from PPh_3), 7.74–7.82 (dd, 6H, *o*-H from PPh_3, *J* = 7.33/7.33). $^{13}C\{^1H,^{31}P\}$ NMR ($CDCl_3$, *δ*): 125.52 (*p*-C–Br from CNR), 127.82 (*o*-CH from CNR), 128.87 (*m*-CH form PPh_3), 129.26 (*ipso*-C from PPh_3), 131.88 (*p*-CH form PPh_3), 132.81 (*m*-CH from CNR), 134.45 (*o*-CH form PPh_3); the signals of isocyanide carbon atom C^0 and the carbon atom C^1 adjacent to the isocyanide group were note detected. $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): 27.76.

***cis*-[$PdCl_2$(CNC_6H_4-4-I)(PPh_3)] (6).** Yield 64 mg (95%). HRESI$^+$-MS (*m/z*): calc. for $C_{26}H_{23}IClNOPPd$ 665.9583, found 665.9303 $[M - Cl + CH_3OH]^+$. IR (KBr, selected bands, cm^{-1}):

ν(C–H) 3077 (m), 3019 (m); ν(C≡N) 2219 (s). ^{1}H NMR ($CDCl_3$, δ): 6.61–6.67 (d, 2H, *o*-H form CNR, J = 8.4 Hz), 7.42–7.49 (m, 6H, *m*-H from PPh_3), 7.50–7.56 (m, 3H, *p*-H from PPh_3), 7.64–7.69 (d, 2H, *m*-H from CNR), 7.73–7.83 (dd, 6H, *o*-H from PPh_3, J = 7.7/7.6 Hz). $^{13}C\{^{1}H,^{31}P\}$ NMR ($CDCl_3$, δ): 97.32 (*p*-C–I from CNR), 127.76 (*o*-CH from CNR), 128.90 (*m*-CH from PPh_3), 129.33 (*ipso*-C from PPh_3), 131.90 (*p*-CH from PPh_3), 134.49 (*o*-CH from PPh_3), 138.76 (*m*-CH from CNR); the signals of isocyanide carbon atom C^0 and the carbon atom C^1 adjacent to the isocyanide group were note detected. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 27.76.

S3. Structure determination of new complexes 4–6

Complexes **4**–**6** were characterized by HRESI$^+$-MS, FTIR and ^{1}H and ^{13}C{^{1}H, ^{31}P} NMR spectroscopies. In addition, the structures of corresponding complexes were established by single-crystal X-ray diffraction. The HR ESI$^+$ mass spectra of **4**–**6** demonstrated the $[M - Cl + MeOH]^+$ ion with the characteristic isotopic distribution. The IR spectra of **4**, **5** and **6** display one stretching vibration due to ν(C≡N) at 2208–2221 cm^{-1} suggesting only one CNR ligand in internal coordination sphere of each compound (the IR spectra in solid state for complexes *cis*–$[PdCl_2(CNC_6H_4X)_2]$, X = Cl, Br, I, display two strong bands in range 2219–2241 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of C≡N bonds of isocyanide moieties [2]). The decrease in the frequency of the ν(CN) band upon isocyanide coordination (ν(CN) band of free CNC_6H_4X, X = Cl, Br, I, is observed at 2125–2129 cm^{-1} [2]) pointed at the increase in the nucleophilic character of the isocyanide carbon atom [7].

Based on the literature data for the previously reported *cis*-$[PdCl_2(CNR)(PPh_3)]$ complexes (^{31}P NMR: 27 ppm) [1] and taking into account that each of the ^{31}P NMR spectra of **4**–**6** gives one signal at 27 ppm, the geometry of **4**–**6** in solution was attributed to the *cis* form.

S5. X-ray structure determination

Table S1. Crystal data and structure refinement for (**1**−**3**)•$2I_2$ at 100 K.

Compound	**1**•$2I_2$	**2**•$2I_2$	**3**•$2I_2$
CCDC code	1970202	1970210	1970215
Empirical formula	$C_{14}H_8Cl_2I_6N_2Pd$	$C_{14}H_8Br_2I_6N_2Pd$	$C_{14}H_8I_8N_2Pd$
Formula weight	1142.92	1231.84	1325.82
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	4.3478(2)	4.3321(2)	4.3477(3)
b (Å)	16.3417(8)	16.4622(8)	16.6599(12)
c (Å)	16.8649(8)	16.8773(6)	17.0264(13)
α (°)	90	90	90
β (°)	91.394(6)	91.431(4)	91.265(7)
γ (°)	90	90	90
Volume (Å^3)	1197.90(10)	1203.24(9)	1232.96(15)
Z	2	2	2
Dc (g·mm^{-3})	3.169	3.400	3.571
F(000)	1008.0	1080.0	1152.0
μ (mm^{-1})	8.732	11.792	10.772
R_1/wR_2, [$I \geq 2\sigma(I)$]	0.0392/0.0808	0.0292/0.0575	0.0422/0.1006
R_1/wR_2, (all data)	0.0517/0.0878	0.0379/0.0611	0.0497/0.1067

Table S2. Crystal data and structure refinement for **4**−**5** at 100 K.

Compound	**4**	**5**	**6**
CCDC code	1580733	1580728	1580740
Empirical formula	$C_{25}H_{19}Cl_3NPPd$	$C_{25}H_{19}BrCl_2NPPd$	$C_{25}H_{19}ICl_2NPPd$
Formula weight	577.13	621.59	668.58
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.3651(2)	9.3603(2)	9.3075(7)
b (Å)	9.6895(2)	9.6681(3)	9.5718(5)
c (Å)	27.0699(7)	27.4300(8)	27.974(3)
α (°)	90	90	90
β (°)	96.090(2)	95.726(3)	94.952(7)
γ (°)	90	90	90
Volume ($Å^3$)	2442.53(10)	2469.92(12)	2482.9(4)
Z	4	4	4
Dc ($g \cdot mm^{-3}$)	1.569	1.672	1.789
F(000)	1152.0	1224.0	1296.0
μ (mm^{-1})	1.166	2.663	2.284
R_1/wR_2, $[I \geq 2\sigma(I)]$	0.0291/0.0621	0.0293/0.0569	0.0383/0.0738
R_1/wR_2, (all data)	0.0368/0.0662	0.0394/0.0610	0.0495/0.0809

Observed difference in absorption coefficient of **6** and **5** could be explained by the shapes and sizes of the crystals.

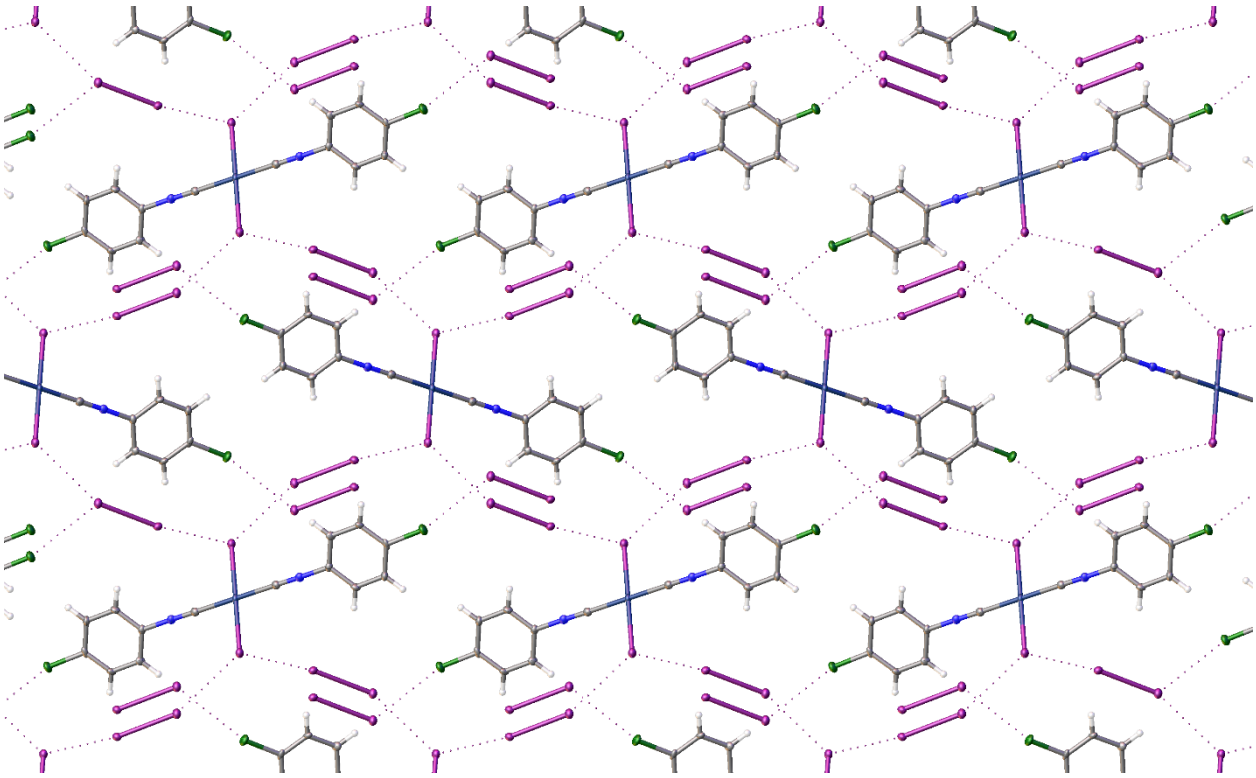


Figure S1. 3D framework of halogen bonded **3**•2I_2. Thermal ellipsoids are drawn with the 50% probability.

Table S3. Geometry parameters of XBs I–I•••I–Pd in (**1**–**3**)•2I_2.

Structure	Pd–X1•••I–I	*d*(I•••I), Å	R_{II}[a]	∠(I–I•••I),°	∠(I•••I–Pd),°
1•2I_2	I2S–I1S•••I1–Pd1	3.3153(7)	0.83	171.331(18)	95.620(14)
	I1S–I2S•••I1–Pd1	3.7639(7)	0.95	157.85(2)	114.712(16)
3•2I_2	I2S–I1S•••I1–Pd1	3.2774(5)	0.82	172.362(16)	95.991(12)
	I1S–I2S•••I1–Pd1	3.8144(5)	0.87	157.384(15)	115.850(12)
3•2I_2	I2S–I1S•••I1–Pd1	3.2475(7)	0.82	173.86(2)	96.874(17)
	I1S–I2S•••I1–Pd1	3.8915(7)	0.98	157.30(18)	117.098(18)
	*Comparison**	*3.96 (I•••I)*	*1.00*	*180*	*90*

[a] $R_{II} = d(\text{I}\bullet\bullet\bullet\text{I})/2r_{vdW}(\text{I})$

Table S4. Geometry parameters of XBs C–X•••I–I in (**1**–**3**)•$2I_2$.

Structure	C–X•••I–I	*d*(X•••I), Å	R_{XI}[a]	∠(C–X•••I),°	∠(X•••I–Pd),°
1•$2I_2$	C5–Cl1•••I2S–I1S	3.7881(18)	1.01	164.1(2)	112.83(3)
2•$2I_2$	C5–Br1•••I2S–I1S	3.7203(6)	0.97	167.78(15)	115.648(15)
3•$2I_2$	C5–I2•••I2S–I1S	3.7124(8)	0.93	171.5(2)	118.37(2)
	*Comparison**	*3.73 (Cl•••I)*	*1.00*	*180*	*90*
		3.83 (Br•••I)			
		3.96 (I•••I)			

[a] $R_{XI} = d(X•••I)/(r_{vdw}(X) + r_{vdw}(I))$, X = Cl, Br, I

Table S5. The characteristic parameters of the stacking interactions in (**1**–**3**)•$2I_2$.*

Crystal	θ,°	h, Å	r, Å	φ,°
1•$2I_2$	0.0(5)	3.426(7)	2.677(9)	0.0(8)
2•$2I_2$	0.0(5)	3.407(5)	2.675(7)	0.0(5)
3•$2I_2$	0.00(7)	3.429(8)	2.673(11)	0.0(11)

*θ is angle between ring planes; h is distances between centroid of one ring to plane of another; r is distances between centroid of one ring and projection of another ring centroid to first plane (shift); φ is twist angle.

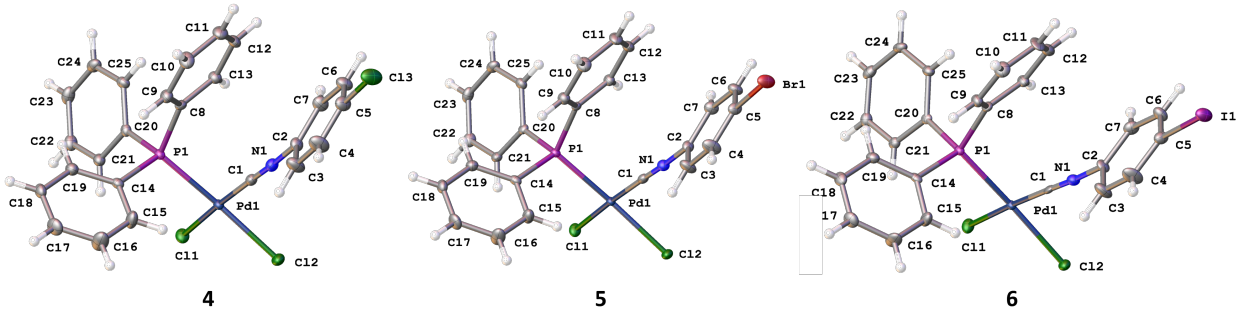


Figure S2. View of complexes **4**–**6** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50 % probability. Hydrogen labels are omitted for simplicity.

In all three structures of **4**–**6** fragments C2–N1–C1–Pd1 are almost linear: the angles Pd1–C1–N1 and C1–N1–C2 found for **4** are 178.1(2)^0 and 176.9(2)^0, respectively, for **5** are 178.2(2)^0 and 176.8(3)^0, respectively, and for **6** are 177.5(4)^0 and 176.8(4)^0, respectively. The distances of Pd1–Cl2 bonds (Pd1–Cl2 2.3511(6) Å for **4**, 2.3569(7) Å for **5** and 2.355(1) Å for **6**) are longer than distances of Pd1–Cl1 bonds (Pd1–Cl1 2.3020(6) Å for **4**, 2.3060(6) Å for **5** and 2.2925(10) Å for **6**), presumably, due to the stronger *trans* influence of the phosphine ligands than that of

CNR [1, 8]. Simultaneously two CN triple bonds of the isocyanide moieties have equal bond lengths in each compound (1.145(3) Å for **4**, 1.146(3) Å for **5** and 1.150(5) Å for **6**), which is typical for other isocyanide complexes [1, 8-12]. In all three structures there are also interactions between one of phenyl rings of PPh_3 and carbon from CN group: distances C1–C8 2.986 Å for **4**, 2.995 Å for **5** and 2.990 Å for **6** are less than the sum of the Bondi's VdW radii: $2R_{VdW}(C) = 3.40$ Å.

In **4**–**6** chlorides are in the *cis*-position [Cl1–Pd1–Cl2 $91.81(2)^0$ for **4**; Cl1–Pd1–Cl2 $91.61(2)^0$ for **5**; Cl1–Pd1–Cl2 $91.30(4)^0$ for **6**], carbons from isocyanides and phosphors from PPh_3 complete the slightly destroyed square planar environment around the metal center.

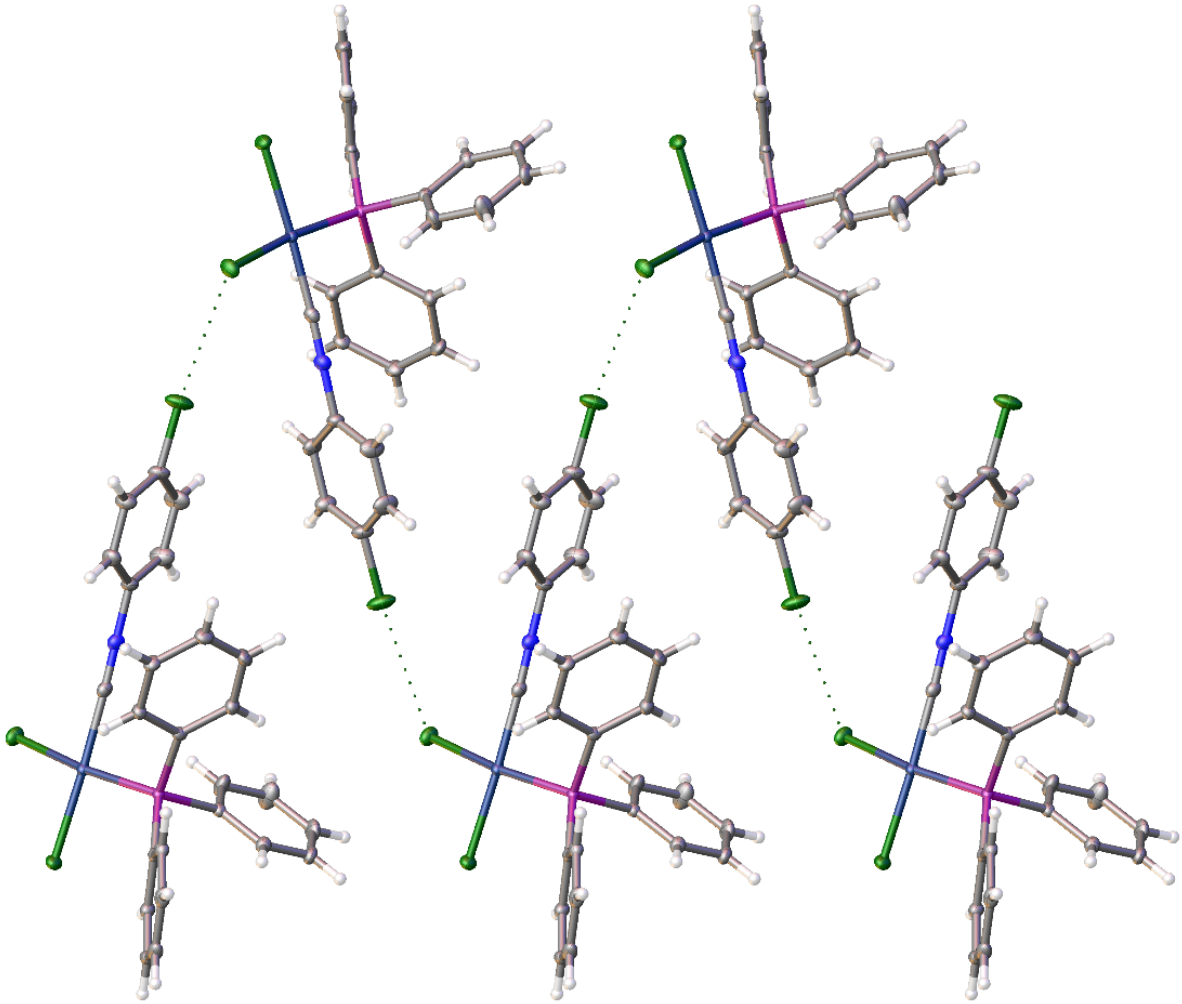


Figure S3. 1D chains of XB-bonded zig-zag like structures of **4**. Thermal ellipsoids are drawn with the 50% probability.

Table S6. Geometry parameters of XBs C5−X•••Cl2 in **4**–**6**.

Structure	C5−X•••Cl2−Pd1	*d*(X•••Cl), Å	R_{XCl}	∠(C−X•••Cl),°	∠(X•••Cl−Pd),°
4	C5−Cl3•••Cl2−Pd1	3.4024(8)	0.97	175.09(10)	111.95(2)
5	C5−Br1•••Cl2−Pd1	3.3593(7)	0.93	174.62(9)	113.01(2)
6	C5−I1•••Cl2−Pd1	3.3633(9)	0.90	173.70(11)	114.21(3)
	Comparison	*3.50 (Cl•••Cl)* *3.60 (Br•••Cl)* *3.73 (I•••Cl)*	*1.00*	*180*	*90*

S5. Computational details

Table S7. Values of the density of all electrons – ρ(**r**), Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, energy density – H_b, potential energy density – V(**r**), and Lagrangian kinetic energy – G(**r**) (Hartree) at the bond critical points (3, –1), corresponding to different non-covalent interactions involving halogen atoms in **1**–**3**•2I_2 and **4**–**6**, bond lengths – *l* (Å), as well as energies for these contacts E_{int} (kcal/mol), defined by different approaches.

Complex	ρ(**r**)	$\nabla^2\rho(\mathbf{r})$	H_b	V(**r**)	G(**r**)	–G(**r**)/V(**r**)	E_{int}[a]	E_{int}[b]	*l*
I2S–I1S•••I1–Pd1									
1•2I_2	0.024	0.050	–0.002	–0.016	0.014	0.9	5.0	3.8	3.315
2•2I_2	0.025	0.051	–0.002	–0.018	0.015	0.8	5.6	4.0	3.277
3•2I_2	0.027	0.052	–0.003	–0.019	0.016	0.8	6.0	4.3	3.247
I1S–I2S•••I1–Pd1									
1•2I_2	0.010	0.032	0.001	–0.006	0.007	1.2	1.9	1.9	3.764
2•2I_2	0.009	0.030	0.001	–0.005	0.006	1.2	1.6	1.6	3.814
3•2I_2	0.008	0.027	0.001	–0.004	0.005	1.2	1.3	1.3	3.891
C–X•••I–I									
1•2I_2	0.006	0.022	0.001	–0.003	0.004	1.2	0.9	1.1	3.788
2•2I_2	0.008	0.026	0.001	–0.004	0.005	1.2	1.3	1.3	3.720
3•2I_2	0.011	0.037	0.001	–0.007	0.008	1.1	2.2	2.2	3.712
C5–X•••Cl2									
4	0.008	0.028	0.001	–0.004	0.006	1.4	1.3	1.6	3.402
5	0.010	0.033	0.001	–0.006	0.007	1.2	1.9	1.9	3.359
6	0.013	0.043	0.001	–0.009	0.010	1.1	2.8	2.7	3.363

[a] $E_{int} = -V(\mathbf{r})/2$ [13]
[b] $E_{int} = 0.429G(\mathbf{r})$ [14]

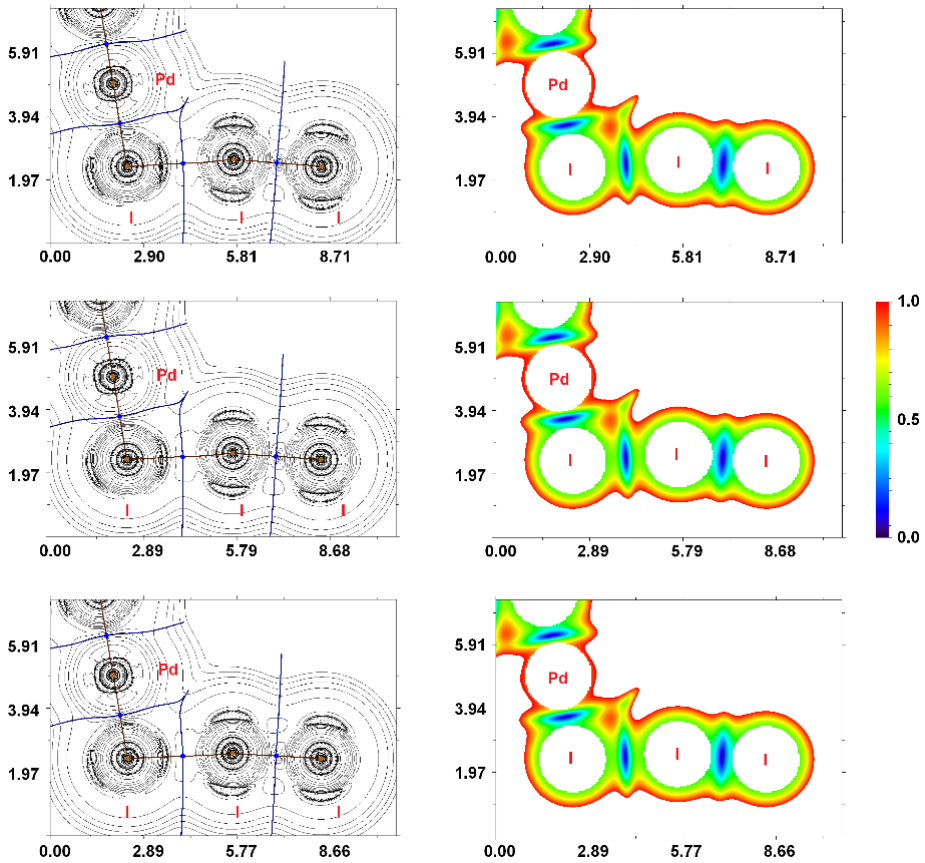


Figure S4. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, bond paths and selected zero-flux surfaces (left) and RDG isosurfaces (right) referring to the I–I•••I–Pd halogen bonding in **1**•2I_2, **2**•2I_2 and **3**•2I_2 (from top to bottom). Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown. Length units – Å, RDG isosurface values are given in Hartree.

Table S8. Maximum electrostatic potentials ($V_S(\mathbf{r})_{max}$, kcal/mol) on the halogen atoms X ("values" of σ-holes) calculated on the 0.001 a.u. molecular surfaces for **1**–**6** model species (ωB97XD/DZP-DKH level of theory) and minimum electrostatic potentials ($V_S(\mathbf{r})_{max}$, kcal/mol) on the iodine atoms calculated on the 0.001 a.u. molecular surfaces for **4**–**6** model species.

Complex	$V_S(\mathbf{r})_{max}$ on X	$V_S(\mathbf{r})_{min}$ on I
1	11.8	–7.8
2	15.8	–8.0
3	22.8	–8.9
4	14.1	
5	17.9	
6	24.0	

Table S9. Cartesian atomic coordinates of model species.

Atom	X	Y	Z
cis-[$PdCl_2(CNC_6H_4pBr)(PPh_3)$]_wB97XD_DZP-DKH (monomer)			
Pd	2.118319	0.505642	16.896361
Br	9.982029	2.653313	20.963311
Cl	1.769804	-1.038741	18.642303
P	2.477737	2.197269	15.411342
Cl	0.186916	-0.165034	15.830291
N	4.694634	1.253953	18.394754
C	0.563464	5.809561	15.580286
H	0.325057	6.487295	14.989390
C	7.091375	1.057690	18.455072
H	7.063113	0.526911	17.691410
C	1.988005	2.026434	13.667583
C	0.624218	1.907516	13.359444
H	-0.000530	1.858209	14.045047
C	5.924703	1.558498	19.018948
C	4.243456	2.634557	15.379682
C	6.517098	1.907516	15.052710
H	7.124585	1.256853	14.781962
C	1.578228	3.659376	15.989956
C	2.912620	2.115380	12.623894
H	3.820488	2.189825	12.811398
C	4.702437	3.865306	15.833839
H	4.099017	4.523704	16.092033
C	0.200783	1.863043	12.037364
H	-0.702991	1.773130	11.837033
C	1.222809	4.683228	15.109753
H	1.428553	4.610717	14.206077
C	8.301530	1.370937	19.063163
H	9.099041	1.039321	18.717632
C	6.974760	3.128597	15.510689
H	7.889289	3.292955	15.557087
C	3.729638	0.997748	17.834153
C	1.259905	3.783128	17.344242
H	1.484743	3.104427	17.939778
C	2.477154	2.093144	11.300450
H	3.091545	2.171455	10.606112
C	5.160867	1.649378	14.995940
H	4.857032	0.819855	14.702812
C	8.312551	2.177256	20.185457
C	6.078440	4.107009	15.898797
H	6.391367	4.927831	16.203934
C	5.924498	2.349348	20.150522
H	5.128043	2.663562	20.513520
C	1.132076	1.952956	11.020422
H	0.848425	1.919118	10.133941
C	7.139671	2.660661	20.727226
H	7.167572	3.198207	21.485156
C	0.261514	5.928479	16.920652
H	-0.175095	6.688392	17.232886
C	0.605481	4.922997	17.803039
H	0.398801	5.008076	18.706715
cis-[$PdCl_2(CNC_6H_4pBr)(PPh_3)$]_wB97XD_DZP-DKH (associate)			

Pd	2.118319	0.505642	16.896361
Br	9.982029	2.653313	20.963311
Cl	1.769804	-1.038741	18.642303
P	2.477737	2.197269	15.411342
Cl	0.186916	-0.165034	15.830291
N	4.694634	1.253953	18.394754
C	0.563464	5.809561	15.580286
H	0.325057	6.487295	14.989390
C	7.091375	1.057690	18.455072
H	7.063113	0.526911	17.691410
C	1.988005	2.026434	13.667583
C	0.624218	1.907516	13.359444
H	-0.000530	1.858209	14.045047
C	5.924703	1.558498	19.018948
C	4.243456	2.634557	15.379682
C	6.517098	1.907516	15.052710
H	7.124585	1.256853	14.781962
C	1.578228	3.659376	15.989956
C	2.912620	2.115380	12.623894
H	3.820488	2.189825	12.811398
C	4.702437	3.865306	15.833839
H	4.099017	4.523704	16.092033
C	0.200783	1.863043	12.037364
H	-0.702991	1.773130	11.837033
C	1.222809	4.683228	15.109753
H	1.428553	4.610717	14.206077
C	8.301530	1.370937	19.063163
H	9.099041	1.039321	18.717632
C	6.974760	3.128597	15.510689
H	7.889289	3.292955	15.557087
C	3.729638	0.997748	17.834153
C	1.259905	3.783128	17.344242
H	1.484743	3.104427	17.939778
C	2.477154	2.093144	11.300450
H	3.091545	2.171455	10.606112
C	5.160867	1.649378	14.995940
H	4.857032	0.819855	14.702812
C	8.312551	2.177256	20.185457
C	6.078440	4.107009	15.898797
H	6.391367	4.927831	16.203934
C	5.924498	2.349348	20.150522
H	5.128043	2.663562	20.513520
C	1.132076	1.952956	11.020422
H	0.848425	1.919118	10.133941
C	7.139671	2.660661	20.727226
H	7.167572	3.198207	21.485156
C	0.261514	5.928479	16.920652
H	-0.175095	6.688392	17.232886
C	0.605481	4.922997	17.803039
H	0.398801	5.008076	18.706715
Pd	12.497192	-4.328408	24.043342
Br	4.633482	-2.180737	19.976392
Cl	12.845707	-5.872791	22.297400
P	12.137774	-2.636781	25.528361
Cl	14.428594	-4.999084	25.109411

N	9.920876	-3.580097	22.544948
C	14.052047	0.975511	25.359417
H	14.290454	1.653245	25.950313
C	7.524136	-3.776360	22.484631
H	7.552397	-4.307139	23.248293
C	12.627505	-2.807616	27.272119
C	13.991292	-2.926534	27.580259
H	14.616041	-2.975841	26.894655
C	8.690808	-3.275552	21.920754
C	10.372054	-2.199493	25.560021
C	8.098413	-2.926534	25.886993
H	7.490926	-3.577197	26.157741
C	13.037283	-1.174674	24.949747
C	11.702891	-2.718670	28.315809
H	10.795022	-2.644225	28.128305
C	9.913073	-0.968744	25.105863
H	10.516493	-0.310346	24.847670
C	14.414727	-2.971007	28.902338
H	15.318501	-3.060920	29.102670
C	13.392702	-0.150822	25.829950
H	13.186957	-0.223333	26.733626
C	6.313981	-3.463113	21.876540
H	5.516470	-3.794729	22.222071
C	7.640751	-1.705453	25.429014
H	6.726222	-1.541095	25.382616
C	10.885873	-3.836302	23.105549
C	13.355605	-1.050922	23.595461
H	13.130768	-1.729623	22.999925
C	12.138357	-2.740906	29.639253
H	11.523965	-2.662595	30.333590
C	9.454644	-3.184672	25.943763
H	9.758478	-4.014195	26.236891
C	6.302959	-2.656794	20.754246
C	8.537070	-0.727041	25.040906
H	8.224144	0.093781	24.735768
C	8.691013	-2.484702	20.789181
H	9.487468	-2.170488	20.426182
C	13.483434	-2.881094	29.919281
H	13.767085	-2.914932	30.805762
C	7.475839	-2.173389	20.212477
H	7.447939	-1.635843	19.454547
C	14.353997	1.094429	24.019051
H	14.790606	1.854342	23.706817
C	14.010029	0.088947	23.136664
H	14.216710	0.174026	22.232988
cis-[$PdCl_2(CNC_6H_4$*p*Cl)(PPh_3)]_wB97XD_DZP-DKH (monomer)			
Pd	2.062012	0.505986	16.688890
Cl	0.129813	-0.166563	15.633738
Cl	1.717616	-1.012843	18.450078
P	2.420528	2.195350	15.204410
Cl	9.769635	2.681182	20.646246
C	3.675688	0.998019	17.617800
N	4.646068	1.253821	18.169332
C	4.648921	3.868048	15.614627
H	4.047558	4.528872	15.870340

C	1.924182	2.033826	13.459373
C	1.528780	3.661662	15.796049
C	2.852017	2.135566	12.417141
H	3.759088	2.218896	12.605292
C	4.184857	2.632637	15.171571
C	7.045598	1.085224	18.220206
H	7.025728	0.553270	17.458451
C	6.917620	3.133584	15.285431
H	7.830719	3.302182	15.329306
C	0.504599	5.811762	15.397675
H	0.253589	6.487120	14.809805
C	6.018623	4.108348	15.671153
H	6.331381	4.930987	15.969933
C	0.143565	1.866198	11.838423
H	-0.760713	1.769303	11.641659
C	8.251390	2.229554	19.935903
C	6.461203	1.904956	14.832146
H	7.068122	1.254790	14.559476
C	5.871502	1.569699	18.779274
C	8.240989	1.409822	18.822073
H	9.039953	1.079410	18.478610
C	5.865465	2.371990	19.897950
H	5.065037	2.683023	20.255141
C	1.068626	1.970844	10.813419
H	0.784559	1.945652	9.929729
C	2.413831	2.110373	11.099548
H	3.029113	2.188858	10.406163
C	0.567818	1.907863	13.154940
H	-0.055375	1.851663	13.843480
C	7.071496	2.704339	20.479091
H	7.091061	3.245983	21.234924
C	0.238628	5.932881	16.749454
H	-0.188997	6.694476	17.070844
C	1.150258	4.676153	14.919896
H	1.329711	4.593792	14.010366
C	5.098046	1.643339	14.784503
H	4.792452	0.813918	14.497566
C	1.246429	3.795377	17.152134
H	1.489544	3.121957	17.743772
C	0.602395	4.931956	17.623453
H	0.416731	5.017223	18.529753
cis-[$PdCl_2(CNC_6H_4pCl)(PPh_3)$]_wB97XD_DZP-DKH_(associate)			
Pd	2.062012	0.505986	16.688890
Cl	0.129813	-0.166563	15.633738
Cl	1.717616	-1.012843	18.450078
P	2.420528	2.195350	15.204410
Cl	9.769635	2.681182	20.646246
C	3.675688	0.998019	17.617800
N	4.646068	1.253821	18.169332
C	4.648921	3.868048	15.614627
H	4.047558	4.528872	15.870340
C	1.924182	2.033826	13.459373
C	1.528780	3.661662	15.796049
C	2.852017	2.135566	12.417141
H	3.759088	2.218896	12.605292

C	4.184857	2.632637	15.171571
C	7.045598	1.085224	18.220206
H	7.025728	0.553270	17.458451
C	6.917620	3.133584	15.285431
H	7.830719	3.302182	15.329306
C	0.504599	5.811762	15.397675
H	0.253589	6.487120	14.809805
C	6.018623	4.108348	15.671153
H	6.331381	4.930987	15.969933
C	0.143565	1.866198	11.838423
H	-0.760713	1.769303	11.641659
C	8.251390	2.229554	19.935903
C	6.461203	1.904956	14.832146
H	7.068122	1.254790	14.559476
C	5.871502	1.569699	18.779274
C	8.240989	1.409822	18.822073
H	9.039953	1.079410	18.478610
C	5.865465	2.371990	19.897950
H	5.065037	2.683023	20.255141
C	1.068626	1.970844	10.813419
H	0.784559	1.945652	9.929729
C	2.413831	2.110373	11.099548
H	3.029113	2.188858	10.406163
C	0.567818	1.907863	13.154940
H	-0.055375	1.851663	13.843480
C	7.071496	2.704339	20.479091
H	7.091061	3.245983	21.234924
C	0.238628	5.932881	16.749454
H	-0.188997	6.694476	17.070844
C	1.150258	4.676153	14.919896
H	1.329711	4.593792	14.010366
C	5.098046	1.643339	14.784503
H	4.792452	0.813918	14.497566
C	1.246429	3.795377	17.152134
H	1.489544	3.121957	17.743772
C	0.602395	4.931956	17.623453
H	0.416731	5.017223	18.529753
Pd	12.360398	-4.338764	23.686806
Cl	14.292597	-5.011313	24.741957
Cl	12.704794	-5.857593	21.925618
P	12.001883	-2.649400	25.171285
Cl	4.652775	-2.163568	19.729449
C	10.746723	-3.846731	22.757895
N	9.776342	-3.590929	22.206363
C	9.773489	-0.976702	24.761068
H	10.374852	-0.315878	24.505355
C	12.498228	-2.810924	26.916323
C	12.893630	-1.183088	24.579647
C	11.570393	-2.709184	27.958554
H	10.663323	-2.625854	27.770403
C	10.237553	-2.212113	25.204124
C	7.376813	-3.759526	22.155490
H	7.396682	-4.291480	22.917245
C	7.504790	-1.711166	25.090265
H	6.591691	-1.542568	25.046390

C	13.917811	0.967012	24.978020
H	14.168821	1.642370	25.565890
C	8.403787	-0.736402	24.704542
H	8.091029	0.086237	24.405762
C	14.278845	-2.978552	28.537272
H	15.183123	-3.075447	28.734037
C	6.171021	-2.615196	20.439792
C	7.961207	-2.939794	25.543549
H	7.354288	-3.589960	25.816220
C	8.550908	-3.275051	21.596421
C	6.181421	-3.434928	21.553623
H	5.382457	-3.765340	21.897086
C	8.556945	-2.472760	20.477745
H	9.357374	-2.161727	20.120555
C	13.353784	-2.873906	29.562277
H	13.637851	-2.899098	30.445966
C	12.008579	-2.734377	29.276148
H	11.393297	-2.655892	29.969533
C	13.854592	-2.936887	27.220756
H	14.477786	-2.993087	26.532215
C	7.350914	-2.140411	19.896604
H	7.331349	-1.598767	19.140771
C	14.183783	1.088131	23.626242
H	14.611407	1.849726	23.304851
C	13.272152	-0.168597	25.455799
H	13.092699	-0.250958	26.365329
C	9.324365	-3.201411	25.591193
H	9.629958	-4.030832	25.878129
C	13.175981	-1.049373	23.223562
H	12.932866	-1.722793	22.631923
C	13.820015	0.087206	22.752243
H	14.005679	0.172473	21.845943
cis-[$PdCl_2(CNC_6H_4$*p*I)(PPh_3)]_wB97XD_DZP-DKH (monomer)			
Pd	-2.400546	0.505295	17.218107
I	5.613276	2.589076	21.433660
Cl	-2.752402	-1.061704	18.940447
P	-2.044548	2.180647	15.731544
Cl	-4.314590	-0.163295	16.148751
C	-0.290082	2.624588	15.701445
C	0.634417	1.638692	15.322418
H	0.333054	0.809774	15.030066
C	-2.955207	3.638241	16.296739
C	0.172763	3.847864	16.149587
H	-0.429624	4.505446	16.409611
C	-3.304685	3.756932	17.633921
H	-3.089404	3.077334	18.232281
C	-3.958405	5.777538	15.865318
H	-4.178133	6.461922	15.275319
C	-1.611925	2.077081	12.953504
H	-0.705065	2.156527	13.143295
C	-2.522590	1.994763	14.000006
C	-3.886992	1.889473	13.687588
H	-4.514079	1.852143	14.372344
C	2.445139	3.118492	15.833268
H	3.358319	3.285042	15.885662

C	-2.030217	2.041665	11.636666
H	-1.410165	2.110582	10.947172
C	-4.298903	5.882828	17.195533
H	-4.752196	6.636129	17.496524
C	-3.288348	4.651895	15.404355
H	-3.063462	4.577235	14.506118
C	1.536704	4.094816	16.209507
H	1.843434	4.921820	16.504367
C	-3.372073	1.903831	11.354068
H	-3.652692	1.852143	10.467815
C	-4.305356	1.841614	12.371587
H	-5.210319	1.767911	12.170647
C	1.986355	1.893302	15.381223
H	2.592876	1.240505	15.116462
N	0.159434	1.260606	18.731147
C	-0.810524	1.008868	18.163165
C	3.767831	2.096224	20.547965
C	1.380302	1.549674	19.357376
C	3.742056	1.316123	19.416739
H	4.534766	0.980152	19.065582
C	2.544918	1.031840	18.806673
H	2.514308	0.503477	18.042768
C	1.376318	2.319247	20.488324
H	0.578592	2.637031	20.843661
C	2.598973	2.615016	21.093930
H	2.630972	3.151994	21.852540
C	-3.974683	4.884490	18.083458
H	-4.203316	4.964893	18.981973
cis-[$PdCl_2(CNC_6H_4pI)(PPh_3)$]_wB97XD_DZP-DKH (associate)			
Pd	-2.400546	0.505295	17.218107
I	5.613276	2.589076	21.433660
Cl	-2.752402	-1.061704	18.940447
P	-2.044548	2.180647	15.731544
Cl	-4.314590	-0.163295	16.148751
C	-0.290082	2.624588	15.701445
C	0.634417	1.638692	15.322418
H	0.333054	0.809774	15.030066
C	-2.955207	3.638241	16.296739
C	0.172763	3.847864	16.149587
H	-0.429624	4.505446	16.409611
C	-3.304685	3.756932	17.633921
H	-3.089404	3.077334	18.232281
C	-3.958405	5.777538	15.865318
H	-4.178133	6.461922	15.275319
C	-1.611925	2.077081	12.953504
H	-0.705065	2.156527	13.143295
C	-2.522590	1.994763	14.000006
C	-3.886992	1.889473	13.687588
H	-4.514079	1.852143	14.372344
C	2.445139	3.118492	15.833268
H	3.358319	3.285042	15.885662
C	-2.030217	2.041665	11.636666
H	-1.410165	2.110582	10.947172
C	-4.298903	5.882828	17.195533
H	-4.752196	6.636129	17.496524

C	-3.288348	4.651895	15.404355
H	-3.063462	4.577235	14.506118
C	1.536704	4.094816	16.209507
H	1.843434	4.921820	16.504367
C	-3.372073	1.903831	11.354068
H	-3.652692	1.852143	10.467815
C	-4.305356	1.841614	12.371587
H	-5.210319	1.767911	12.170647
C	1.986355	1.893302	15.381223
H	2.592876	1.240505	15.116462
N	0.159434	1.260606	18.731147
C	-0.810524	1.008868	18.163165
C	3.767831	2.096224	20.547965
C	1.380302	1.549674	19.357376
C	3.742056	1.316123	19.416739
H	4.534766	0.980152	19.065582
C	2.544918	1.031840	18.806673
H	2.514308	0.503477	18.042768
C	1.376318	2.319247	20.488324
H	0.578592	2.637031	20.843661
C	2.598973	2.615016	21.093930
H	2.630972	3.151994	21.852540
C	-3.974683	4.884490	18.083458
H	-4.203316	4.964893	18.981973
Pd	8.085925	-4.280605	24.586268
I	0.072103	-2.196824	20.370714
Cl	8.437781	-5.847604	22.863927
P	7.729926	-2.605253	26.072831
Cl	9.999968	-4.949195	25.655624
C	5.975461	-2.161312	26.102930
C	5.050962	-3.147208	26.481957
H	5.352324	-3.976126	26.774309
C	8.640586	-1.147659	25.507636
C	5.512616	-0.938036	25.654787
H	6.115002	-0.280454	25.394764
C	8.990064	-1.028968	24.170453
H	8.774783	-1.708566	23.572094
C	9.643784	0.991638	25.939057
H	9.863512	1.676022	26.529056
C	7.297304	-2.708819	28.850871
H	6.390444	-2.629373	28.661079
C	8.207968	-2.791137	27.804368
C	9.572370	-2.896427	28.116786
H	10.199458	-2.933757	27.432031
C	3.240239	-1.667408	25.971107
H	2.327059	-1.500858	25.918712
C	7.715596	-2.744235	30.167709
H	7.095543	-2.675318	30.857203
C	9.984281	1.096928	24.608842
H	10.437575	1.850229	24.307851
C	8.973726	-0.134005	26.400020
H	8.748840	-0.208665	27.298257
C	4.148674	-0.691084	25.594868
H	3.841944	0.135920	25.300008
C	9.057451	-2.882069	30.450307

H	9.338070	-2.933757	31.336559
C	9.990735	-2.944286	29.432788
H	10.895698	-3.017989	29.633728
C	3.699023	-2.892598	26.423152
H	3.092503	-3.545395	26.687913
N	5.525944	-3.525294	23.073228
C	6.495903	-3.777032	23.641210
C	1.917547	-2.689676	21.256410
C	4.305076	-3.236226	22.446998
C	1.943322	-3.469777	22.387636
H	1.150612	-3.805748	22.738793
C	3.140461	-3.754060	22.997701
H	3.171070	-4.282423	23.761607
C	4.309061	-2.466653	21.316051
H	5.106787	-2.148869	20.960714
C	3.086406	-2.170884	20.710445
H	3.054406	-1.633906	19.951835
C	9.660062	0.098590	23.720917
H	9.888695	0.178993	22.822402
trans-[$PdI_2(CNC_6H_4pBr)_2$]_wB97XD_DZP-DKH (monomer)			
I	0.374892	8.381729	10.965474
Pd	-0.210739	8.231100	8.436018
Br	3.837796	16.157485	6.437694
N	1.336665	10.893038	7.968663
C	0.783922	9.902013	8.140758
C	1.980300	12.107948	7.678464
C	3.393649	13.373891	6.247715
H	3.968739	13.433698	5.519062
C	3.112230	14.491675	6.986710
C	2.827805	12.160627	6.580094
H	3.008669	11.397802	6.079670
C	1.714289	13.229024	8.459639
H	1.158076	13.169678	9.203004
C	2.294978	14.425826	8.105326
H	2.139235	15.188553	8.614980
I	-0.796370	8.080471	5.906562
Br	-4.259274	0.304715	10.434342
N	-1.758143	5.569162	8.903374
C	-1.205400	6.560187	8.731279
C	-2.401778	4.354252	9.193573
C	-3.815127	3.088309	10.624321
H	-4.390217	3.028502	11.352974
C	-3.533708	1.970525	9.885326
C	-3.249283	4.301573	10.291942
H	-3.430147	5.064398	10.792367
C	-2.135767	3.233176	8.412397
H	-1.579554	3.292522	7.669032
C	-2.716456	2.036374	8.766710
H	-2.560713	1.273647	8.257057
trans-[$PdI_2(CNC_6H_4pBr)_2$]•$2I_2$_wB97XD_DZP-DKH (associate)			
I	-0.766258	11.423121	11.400266
I	-1.636798	13.923070	12.116653
I	0.374892	8.381729	10.965474
Pd	-0.210739	8.231100	8.436018
Br	3.837796	16.157485	6.437694

N	1.336665	10.893038	7.968663
C	0.783922	9.902013	8.140758
C	1.980300	12.107948	7.678464
C	3.393649	13.373891	6.247715
H	3.968739	13.433698	5.519062
C	3.112230	14.491675	6.986710
C	2.827805	12.160627	6.580094
H	3.008669	11.397802	6.079670
C	1.714289	13.229024	8.459639
H	1.158076	13.169678	9.203004
C	2.294978	14.425826	8.105326
H	2.139235	15.188553	8.614980
I	-0.796370	8.080471	5.906562
Br	-4.259274	0.304715	10.434342
N	-1.758143	5.569162	8.903374
C	-1.205400	6.560187	8.731279
C	-2.401778	4.354252	9.193573
C	-3.815127	3.088309	10.624321
H	-4.390217	3.028502	11.352974
C	-3.533708	1.970525	9.885326
C	-3.249283	4.301573	10.291942
H	-3.430147	5.064398	10.792367
C	-2.135767	3.233176	8.412397
H	-1.579554	3.292522	7.669032
C	-2.716456	2.036374	8.766710
H	-2.560713	1.273647	8.257057
I	4.676880	21.501279	5.471770
I	5.547420	19.001330	4.755383
I	-5.098358	-5.039079	11.400266
I	-5.968898	-2.539130	12.116653
I	1.610531	13.270179	2.964248
I	0.739991	10.770230	3.680635
I	0.344780	5.039079	5.471770
I	1.215320	2.539130	4.755383
I	-2.032009	3.192021	13.907788
I	-1.161469	5.691970	13.191402
trans-[$PdI_2(CNC_6H_4pCl)_2$]_wB97XD_DZP-DKH (monomer)			
I	0.430788	7.999426	10.953714
Pd	-0.205140	8.170850	8.429954
Cl	3.829651	0.356903	6.552604
N	1.325732	5.497348	7.929215
C	0.768301	6.486021	8.109616
C	3.397223	3.001970	6.241538
H	3.971449	2.939284	5.512465
C	1.973514	4.278257	7.662829
C	2.810711	4.207988	6.545017
H	2.966891	4.958987	6.018566
C	3.143545	1.897271	7.000234
C	1.732887	3.168656	8.456930
H	1.174535	3.235085	9.198176
C	2.327512	1.965907	8.141650
H	2.191172	1.214286	8.672754
I	-0.841069	8.342274	5.906195
Cl	-4.239932	15.984797	10.307305
N	-1.736012	10.844352	8.930694

C	-1.178582	9.855679	8.750293
C	-3.807504	13.339730	10.618371
H	-4.381729	13.402416	11.347444
C	-2.383795	12.063443	9.197080
C	-3.220992	12.133712	10.314892
H	-3.377172	11.382713	10.841343
C	-3.553825	14.444429	9.859675
C	-2.143168	13.173044	8.402979
H	-1.584816	13.106615	7.661733
C	-2.737793	14.375793	8.718259
H	-2.601452	15.127414	8.187155
trans-[$PdI_2(CNC_6H_4pCl)_2$]•$2I_2$_wB97XD_DZP-DKH (associate)			
I	-0.766476	4.937808	11.382967
I	-1.655266	2.452236	12.137448
I	0.430788	7.999426	10.953714
Pd	-0.205140	8.170850	8.429954
Cl	3.829651	0.356903	6.552604
N	1.325732	5.497348	7.929215
C	0.768301	6.486021	8.109616
C	3.397223	3.001970	6.241538
H	3.971449	2.939284	5.512465
C	1.973514	4.278257	7.662829
C	2.810711	4.207988	6.545017
H	2.966891	4.958987	6.018566
C	3.143545	1.897271	7.000234
C	1.732887	3.168656	8.456930
H	1.174535	3.235085	9.198176
C	2.327512	1.965907	8.141650
H	2.191172	1.214286	8.672754
I	-0.841069	8.342274	5.906195
Cl	-4.239932	15.984797	10.307305
N	-1.736012	10.844352	8.930694
C	-1.178582	9.855679	8.750293
C	-3.807504	13.339730	10.618371
H	-4.381729	13.402416	11.347444
C	-2.383795	12.063443	9.197080
C	-3.220992	12.133712	10.314892
H	-3.377172	11.382713	10.841343
C	-3.553825	14.444429	9.859675
C	-2.143168	13.173044	8.402979
H	-1.584816	13.106615	7.661733
C	-2.737793	14.375793	8.718259
H	-2.601452	15.127414	8.187155
I	4.703996	-4.937808	5.476941
I	5.592785	-2.452236	4.722460
I	-5.114276	21.279508	11.382967
I	-6.003066	18.793936	12.137448
I	0.356196	11.403892	5.476941
I	1.244985	13.889464	4.722460
I	1.612564	3.233042	2.953013
I	0.723774	5.718614	3.707494
I	-2.022845	13.108658	13.906896
I	-1.134055	10.623086	13.152415
trans-[$PdI_2(CNC_6H_4pI)_2$]_wB97XD_DZP-DKH (monomer)			
I	-0.723300	8.199500	5.967800

I	3.915100	16.397300	6.383300
Pd	-0.187900	8.330000	8.511100
N	1.371100	10.988900	8.058300
C	0.804400	10.009300	8.228600
C	2.846200	12.228400	6.667600
H	3.017300	11.454500	6.179500
C	3.135900	14.590700	7.054000
C	1.743100	13.329600	8.540100
H	1.194900	13.276800	9.289100
C	2.010900	12.203400	7.772400
C	3.414900	13.429500	6.310100
H	3.985400	13.473300	5.577600
C	2.312300	14.532400	8.162200
H	2.140800	15.303300	8.654000
I	0.347400	8.460400	11.054400
I	-4.290900	0.262600	10.638900
N	-1.747000	5.671000	8.963900
C	-1.180200	6.650600	8.793700
C	-3.222000	4.431500	10.354600
H	-3.393200	5.205400	10.842700
C	-3.511800	2.069200	9.968200
C	-2.119000	3.330300	8.482200
H	-1.570800	3.383100	7.733200
C	-2.386800	4.456500	9.249900
C	-3.790800	3.230400	10.712100
H	-4.361300	3.186600	11.444600
C	-2.688200	2.127500	8.860100
H	-2.516600	1.356600	8.368300
trans-[$PdI_2(CNC_6H_4pI)_2$]•$2I_2$_wB97XD_DZP-DKH (associate)			
I	0.363300	5.175700	5.496500
I	-0.723300	8.199500	5.967800
I	1.227700	2.662600	4.812200
I	3.915100	16.397300	6.383300
Pd	-0.187900	8.330000	8.511100
N	1.371100	10.988900	8.058300
C	0.804400	10.009300	8.228600
C	2.846200	12.228400	6.667600
H	3.017300	11.454500	6.179500
C	3.135900	14.590700	7.054000
C	1.743100	13.329600	8.540100
H	1.194900	13.276800	9.289100
C	2.010900	12.203400	7.772400
C	3.414900	13.429500	6.310100
H	3.985400	13.473300	5.577600
C	2.312300	14.532400	8.162200
H	2.140800	15.303300	8.654000
I	-0.739200	11.484200	11.525800
I	0.347400	8.460400	11.054400
I	-1.603600	13.997300	12.210100
I	-4.290900	0.262600	10.638900
N	-1.747000	5.671000	8.963900
C	-1.180200	6.650600	8.793700
C	-3.222000	4.431500	10.354600
H	-3.393200	5.205400	10.842700
C	-3.511800	2.069200	9.968200

C	-2.119000	3.330300	8.482200
H	-1.570800	3.383100	7.733200
C	-2.386800	4.456500	9.249900
C	-3.790800	3.230400	10.712100
H	-4.361300	3.186600	11.444600
C	-2.688200	2.127500	8.860100
H	-2.516600	1.356600	8.368300
I	4.711000	21.835600	5.496500
I	5.575400	19.322500	4.812200
I	-5.086900	-5.175700	11.525800
I	-5.951300	-2.662600	12.210100
I	1.622600	13.505700	3.014600
I	0.758200	10.992500	3.698900
I	-1.998500	3.154200	14.007600
I	-1.134100	5.667400	13.323300

S6. Relative literature data of Cl/Br/I triple halogen isostructural exchange

The triple Cl/Br/I isomorphous series:

(i) the 1:1 cocrystals of 4,4'-azopyridine and 4,6-dihalobenzene-1,3-diol (X = Cl, Br, I) [15]

The cocrystals of 4,4'-azopyridine (**4,4'-AP**) and 4,6-diXbenzene-1,3-diol (**4,6-diX-res**; X = Cl, Br, I) with the ratio 1:1 were obtained from equimolar solutions of these reagents by slow evaporation. Each of the obtained structure is defined by a discrete four-component supramolecular fragment 2(**4,6-diX-res**)•2(**4,4'-AP**) and assembled by halogen bonding (XBs X•••O highlighted in red, **Fig. S5**) and hydrogen bonding (HBs N•••H and X•••H are present in **Fig. S7** as dashed black lines). The parameters of XBs are present in **Table S10**.

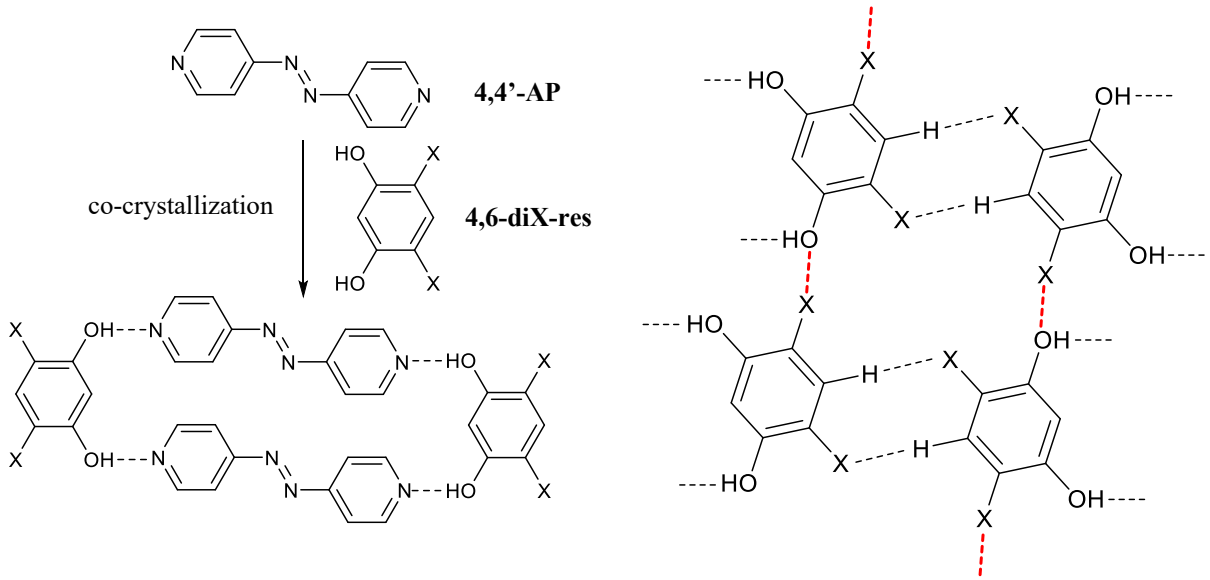


Figure S5. Isostructural cocrystals of 4,4'-azopyridine (**4,4'-AP**) and 4,6-diXbenzene-1,3-diol (**4,6-diX-res**; X = Cl, Br, I) in a 1:1 ratio. All the three structures are isostructural and preserve XB (dashed red lines) and HB (dashed black lines).

Table S10. XB parameters in (**4,6-diX-res**)•(**4,4'-AP**), X = Cl **8**, Br **9**, I **10**.

CCDC Identifier	X•••O	*d*(X•••O), Å	R_{XO} (Bondi)	R_{XO} (Rowland)	R_{XO} (Alvarez)	R_{XO} (Batsanov)	∠(C–X•••O),°	∠(X•••O–C),°
1059604	Cl•••O	3.2171(17)	0.984	0.963	0.969	0.960	160.59(6)	162.39(11)
1059606	Br•••O	3.1513(19)	0.935	0.913	0.938	0.913	156.75(6)	158.42(12)
1059608	I•••I	3.227(2)	0.922	0.894	0.912	0.884	152.32(6)	154.14(14)
	X•••O		Σr_{vdW}, Å (Bondi)	Σr_{vdW}, Å (Rowland)	Σr_{vdW}, Å (Alvarez)	Σr_{vdW}, Å (Batsanov)	Comparative ∠(C–X•••O),°	
	Cl•••O		3.27	3.34	3.32	3.35	180	
	Br•••O		3.37	3.45	3.36	3.45	180	
	I•••O		3.50	3.61	3.54	3.65	180	

(ii) the crystals of 2-acetoxy-5-halobenzoic acid (X = Cl, Br, I) [16]

Crystals of 2-acetoxy-5-chlorobenzoic and 2-acetoxy-5-iodobenzoic acids suitable for XRD were obtained by slow evaporation of their concentrated solutions in a 1:1 mixture of H_2O and CH_3CN, crystals of 5-bromo derivative were obtained by slow evaporation of its concentrated solution in a 1:1 mixture of H_2O and CH_3OH. In the structures of substituted aspirins form 1D chains from hydrogen bonded dimers which in turn are linked together by the halogen bonds between X (X = Cl, Br, I) and carbonyl oxygen (**Fig. S6**). Each such chain is linked with four another ones, which are perpendicular to the former, by hydrogen bonds.

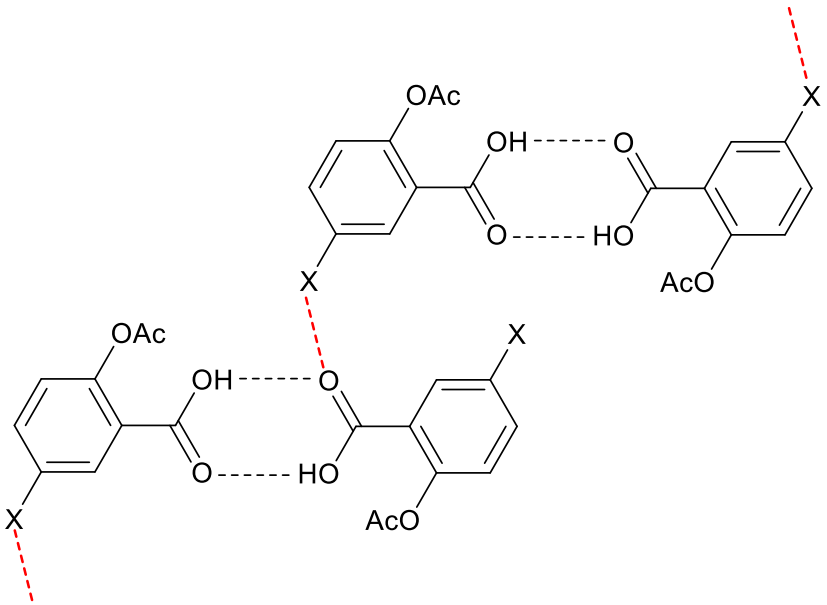


Figure S6. Fragment of the 1D chain of the structures of 2-acetoxy-5-halobenzoic acids (X = Cl, Br, I). The halogen bonds are designated as red dotted lines.

Table S11. XB parameters of the structures of 2-acetoxy-5-halobenzoic acids (X = Cl, Br, I).

CCDC Identifier	**X•••O**	*d*(X•••X), Å	R_{XX} (Bondi)	R_{XX} (Rowland)	R_{XX} (Alvarez)	R_{XX} (Batsanov)	∠(C–X•••O),°	∠(X•••O–C),°
643152	Cl•••O	3.1209(13)	0.954	0.934	0.940	0.932	154.98(7)	147.87(11)
643151	Br•••O	3.1985(18)	0.949	0.927	0.952	0.927	156.19(10)	146.68(19)
643154	I•••O	3.375(3)	0.964	0.935	0.953	0.925	157.00(12)	145.3(3)
	X•••O		Σr_{vdW}, Å (Bondi)	Σr_{vdW}, Å (Rowland)	Σr_{vdW}, Å (Alvarez)	Σr_{vdW}, Å (Batsanov)	Comparative ∠(C–X•••O),°	Comparative ∠(X•••O–C),°
	Cl•••O		3.27	3.34	3.32	3.35	180	90
	Br•••O		3.37	3.45	3.36	3.45	180	90
	I•••O		3.50	3.61	3.54	3.65	180	90

(iii) the crystals of 1,3,5-triethyl-2,4,6-(4-halophenoxymethyl)benzenes (X = Cl, Br, I) [17]

The crystals of 1,3,5-triethyl-2,4,6-(4-Xphenoxy)methylbenzenes (X = Cl, Br, I) were studied. Diffraction quality crystals of bromo- and iododerivatives were obtained by dissolving the compounds in acetonitrile and then slow evaporation of the solvent, crystals of chloroderivative were obtained by slow evaporation of chloroform from its solution of this substance. All the structures are assembled by X•••X and X•••*pi* halogen bonds (**Fig. S7**, **Table S12**). Despite the fact that bromo and chloro analogues are isostructural to idodo derivative structure, which crystallizes in $P2_1/n$ space group, they crystallize in the $P2_1/c$ space group. Also all the structures are isomorphous despite the different molecular conformations.

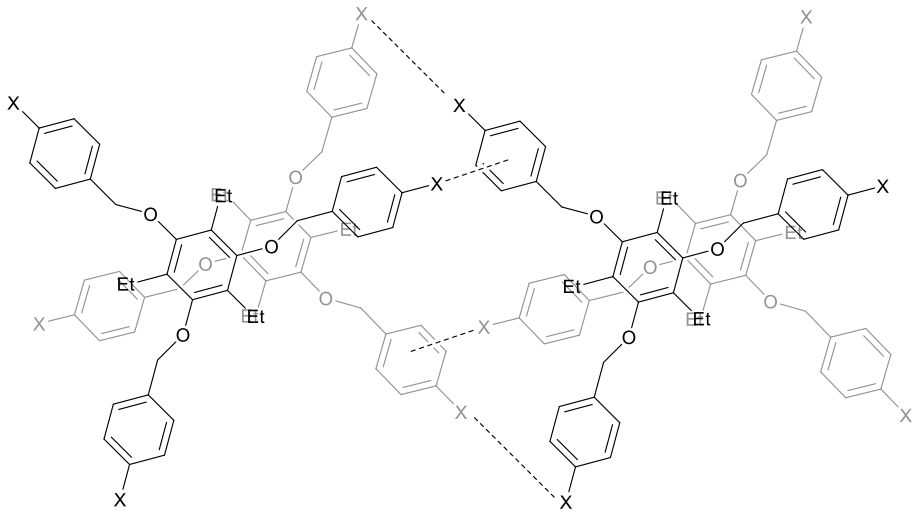


Figure S7. Fragment of the crystal structure of the crystals of 1,3,5-triethyl-2,4,6-(4-Xphenoxy)methylbenzenes (X = Cl, Br, I). The X•••X and X•••*pi* halogen bonds are designated as dotted lines. The grey structures are at the back, black are at the front.

Table S12. XB parameters in 2,4,6-triethyl-1,3,5-tris(4-Xphenoxy)methylbenzenes, X = Cl, Br, I

CCDC Identifier	**X•••X**	*d*(X•••X), Å	R_{XX} (Bondi)	R_{XX} (Rowland)	R_{XX} (Alvarez)	R_{XX} (Batsanov)	∠(C–X•••X),°	∠(X•••X–C),°
962405	Cl•••Cl	3.6194(9)	1.034	1.028	0.994	1.005	161.93(6)	91.44(8)
962411	Br•••Br	3.6623(9)	0.990	0.979	0.984	0.964	163.55(12)	89.14(18)
962417	I•••I	3.9174(4)	0.989	0.965	0.960	0.933	168.50(11)	86.04(12)
	X•••X		Σr_{vdW}, Å (Bondi)	Σr_{vdW}, Å (Rowland)	Σr_{vdW}, Å (Alvarez)	Σr_{vdW}, Å (Batsanov)	Comparative ∠(C–X•••X),°	Comparative ∠(X•••X–C),°
	Cl•••Cl		3.50	3.52	3.64	3.6	180	90
	Br•••Br		3.70	3.74	3.72	3.8	180	90
	I•••I		3.96	4.06	4.08	4.2	180	90

(iv) trihalomesitylenes (X = Cl, Br, I) [18]

Unusual melting points of trihalomesitylenes (X = Cl, Br, I) led Saraswatula to the study of their crystals. The structures of these solid substances consist of two-dimensional layers connected with each other by *pi-pi* stacking and weak hydrogen bonds. In each 2D layer every three molecules of trihalomesitylene next to each other are connected by three XBs X•••X (**Fig. S8**) which are different in energy due to different relative lengths (in the **Table S13** only the data for the strongest XBs are presented; these XBs are structurally equivalent in all of the three structures). Single crystals of bromo- and iododerivatives were produced from ethyl acetate, chloroderivative was produced from dichloromethane solution using the method of slow evaporation of the solvent at room temperature.

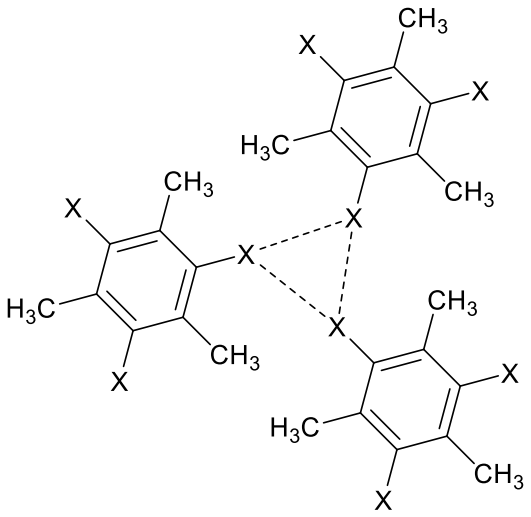


Figure S8. Fragment of 2D layer of the crystal of trihalomesitylene (in the figure X = Cl, Br, I). XB are designated as dotted lines.

Table S13. XB parameters in triXmesitylenes, X = Cl, Br, I.

CCDC Identifier	**X•••X**	*d*(X•••X), Å	R_{XX} (Bondi)	R_{XX} (Rowland)	R_{XX} (Alvarez)	R_{XX} (Batsanov)	∠(C–X•••X),°	∠(X•••X–C),°
1057999	Cl•••Cl	3.5285(10)	1.008	1.002	0.969	0.980	172.13(10)	128.07(7)
1057994	Br•••Br	3.5847(9)	0.969	0.958	0.964	0.943	175.00(16)	124.98(13)
1058004	I•••I	3.8304(7)	0.967	0.943	0.939	0.912	137.90(12)	120.00(19)
	X•••X		Σr_{vdW}, Å (Bondi)	Σr_{vdW}, Å (Rowland)	Σr_{vdW}, Å (Alvarez)	Σr_{vdW}, Å (Batsanov)	Comparative ∠(C–X•••X),°	Comparative ∠(X•••X–C),°
	Cl•••Cl		3.50	3.52	3.64	3.6	180	90
	Br•••Br		3.70	3.74	3.72	3.8	180	90
	I•••I		3.96	4.06	4.08	4.2	180	90

(v) the crystal structures of Cl_2, Br_2, and I_2 [19, 20] obtained at similar, albeit not exactly the same, temperatures (100 K for Cl_2, 80 K for Br_2, 110 K for I_2).

The crystal structures of dihalogens (Cl_2, Br_2 and I_2) corresponding to very close temperatures can be found in literature (100 K for Cl_2, 80 K for Br_2, 110 K for I_2). All the three structures consist of 2D layers in each of which every molecule of dihalogen is bonded to four other ones by equal XBs (**Fig. S15**, **Table S14**). Single crystals of Cl_2 and Br_2 suitable for XRD were obtained by the corresponding cryogrinding technique.

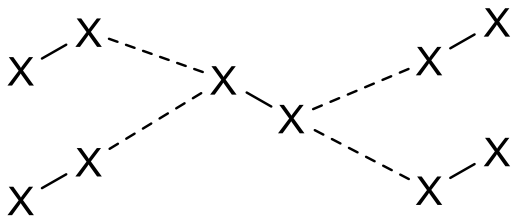


Figure S9. Fragment of the 2D layer of the structures of X_2 (X = Cl, Br, I). All the halogen bonds are designated as dotted lines and are equal to each other.

Table S14. XB parameters in dihalogens.

CCDC Identifier	**X•••X**	*d*(X•••X), Å	R_{XX} (Bondi)	R_{XX} (Rowland)	R_{XX} (Alvarez)	R_{XX} (Batsanov)	∠(X–X•••X),°	∠(X•••X–X),°
1706348	Cl•••Cl	3.29611(6)	0.942	0.936	0.906	0.916	170.67019(8)	104.2717(18)
1706343	Br•••Br	3.30263(12)	0.893	0.883	0.888	0.869	169.87864(18)	104.393(4)
1629598	I•••I	3.5016(16)	0.884	0.862	0.858	0.834	170.14(6)	105.72(4)
	X•••X		Σr_{vdW}, Å (Bondi)	Σr_{vdW}, Å (Rowland)	Σr_{vdW}, Å (Alvarez)	Σr_{vdW}, Å (Batsanov)	Comparative ∠(X–X•••X),°	Comparative ∠(X•••X–X),°
	Cl•••Cl		3.50	3.52	3.64	3.6	180	90
	Br•••Br		3.70	3.74	3.72	3.8	180	90
	I•••I		3.96	4.06	4.08	4.2	180	90

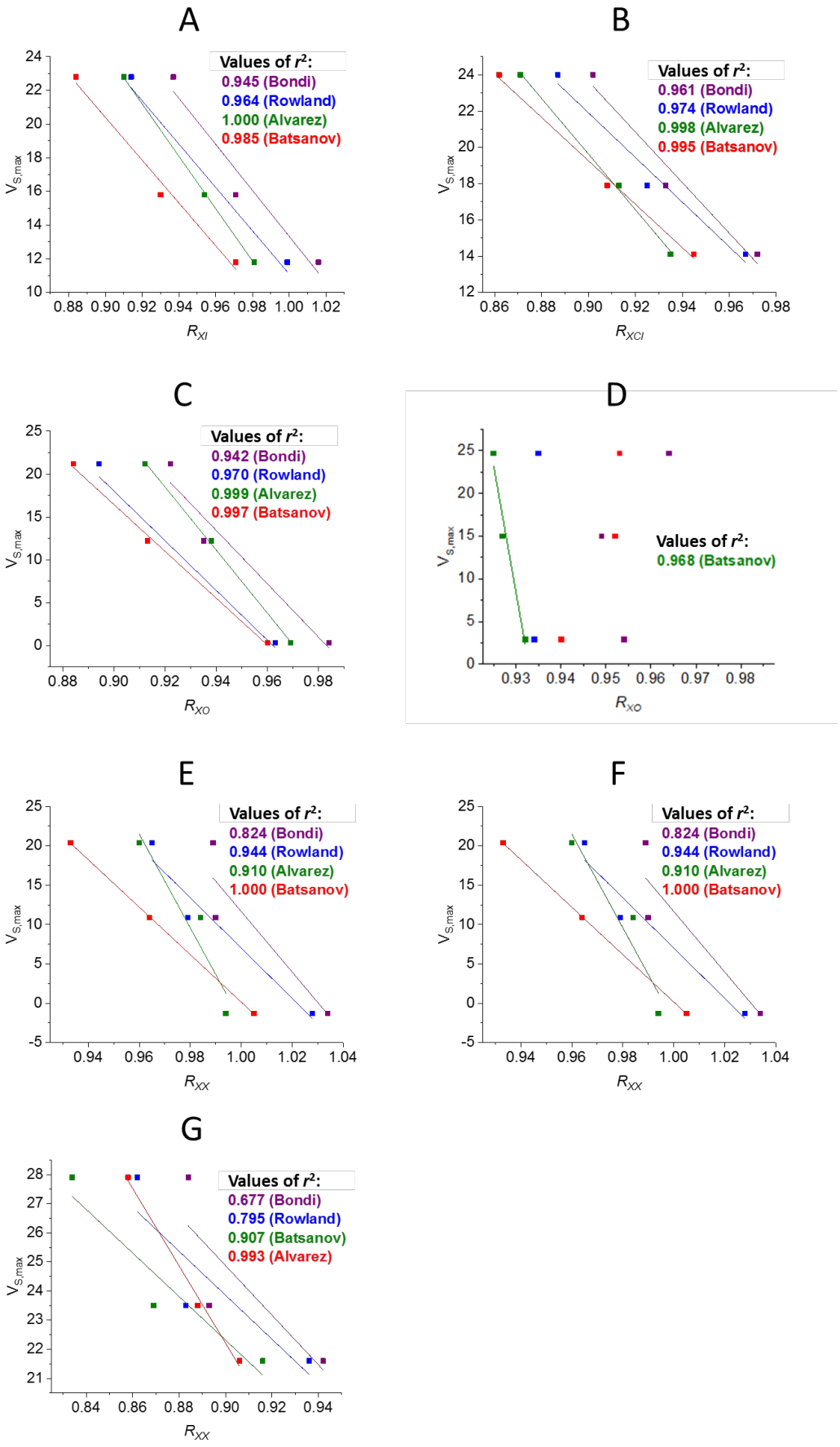


Fig. S10. Dependencies of $V_{S,max}$ on R_{XY} (X = Cl, Br, I) with linear approximation: A. for structures of (**1**–**3**)•2I_2, Y = I; B. for structures of **4**–**6**, Y = Cl; C. for series (*i*), Y = O; D. for series (*ii*), Y = X; E. for series (*iii*), Y = X; F. for series (*iv*), Y = X; G. for series (*v*), Y = X.

S7. Copies of ^{1}H NMR,$^{13}C\{^{1}H,^{31}P\}$ NMR, $^{31}P\{^{1}H\}$ NMR, IR and HR ESI-MS spectra

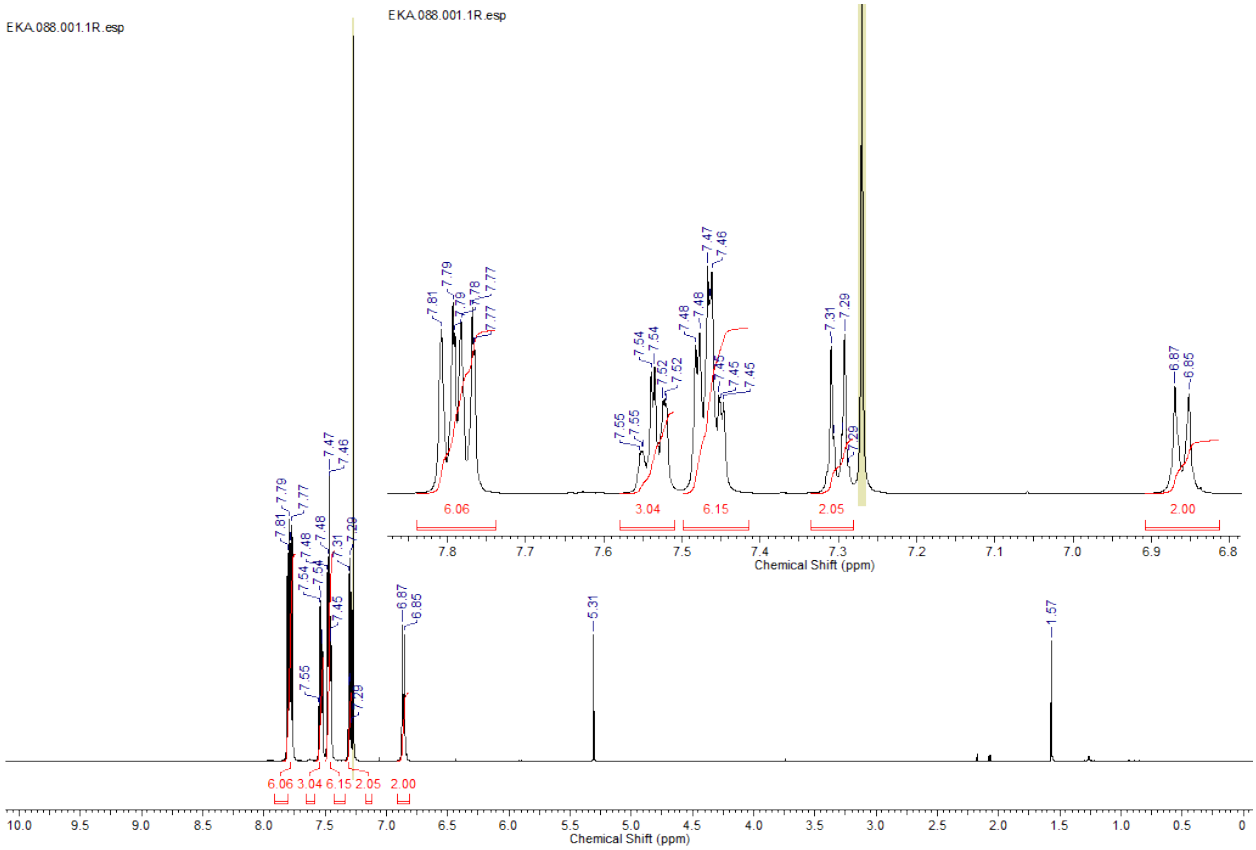


Figure S11. ^{1}H NMR spectrum of **4** ($CDCl_3$).

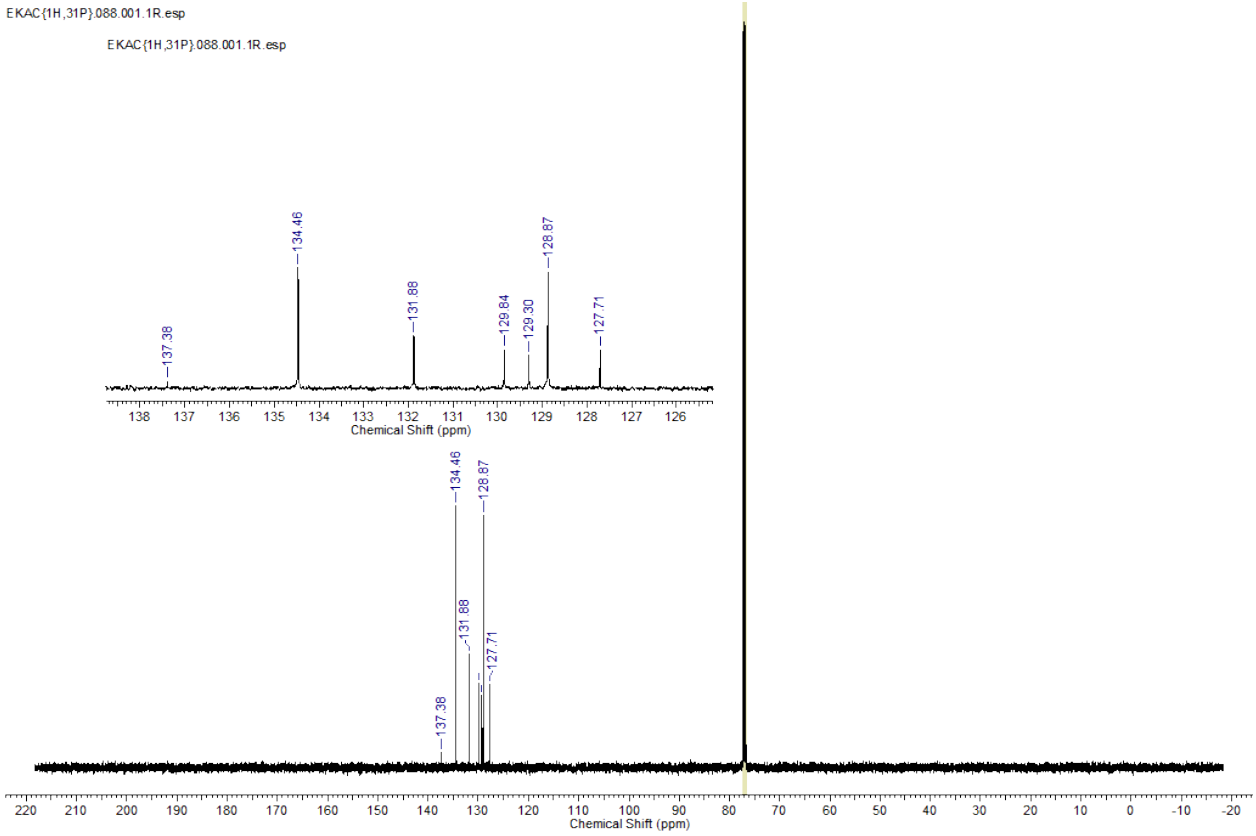


Figure S12. C{^{1}H,^{31}P} NMR spectrum of **4** ($CDCl_3$).

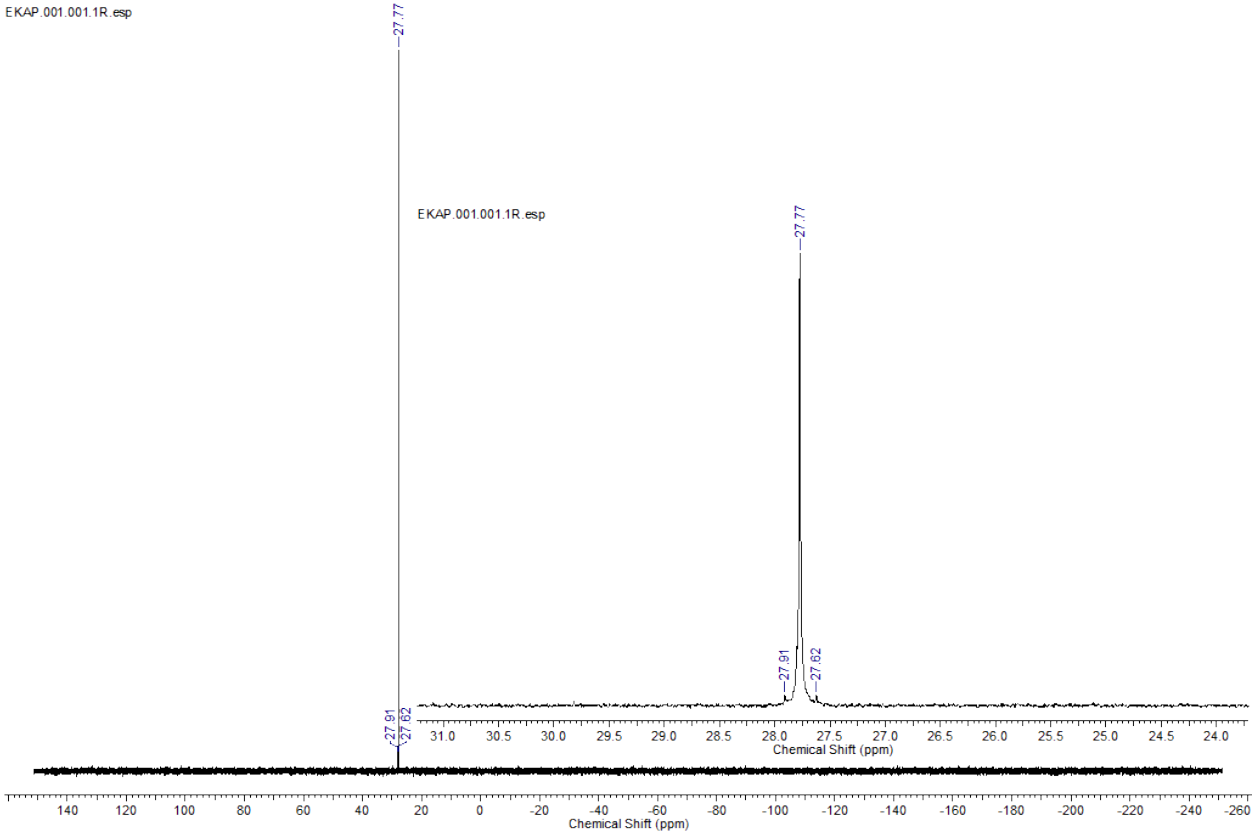


Figure S13. ^{31}P{^{1}H} NMR spectrum of **4** ($CDCl_3$).

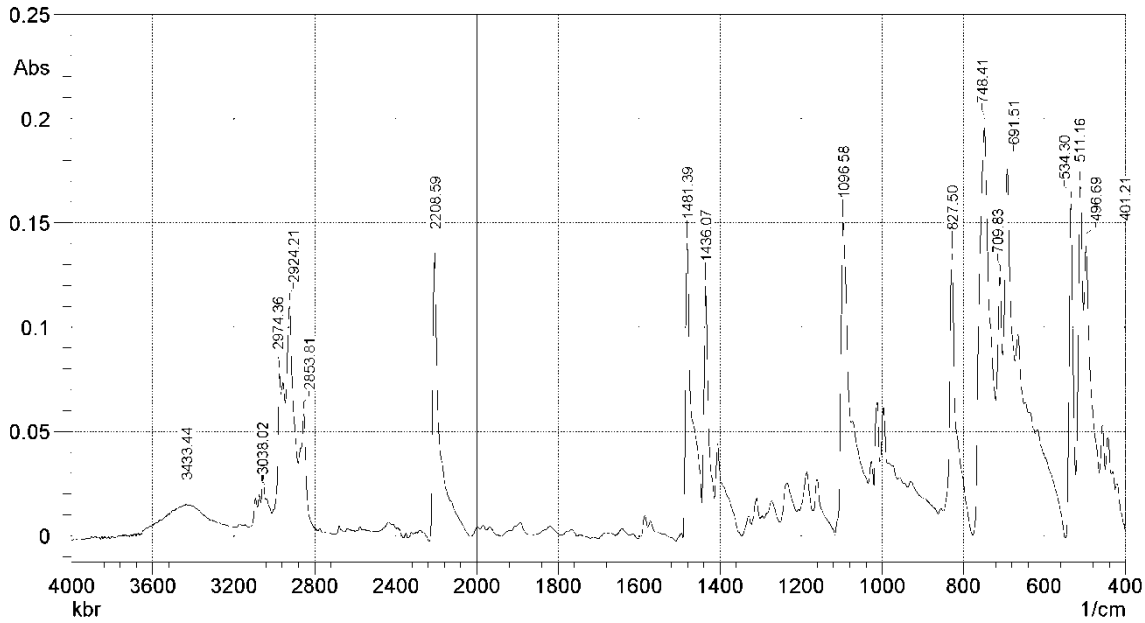


Figure S14. IR spectrum of **4** (KBr).

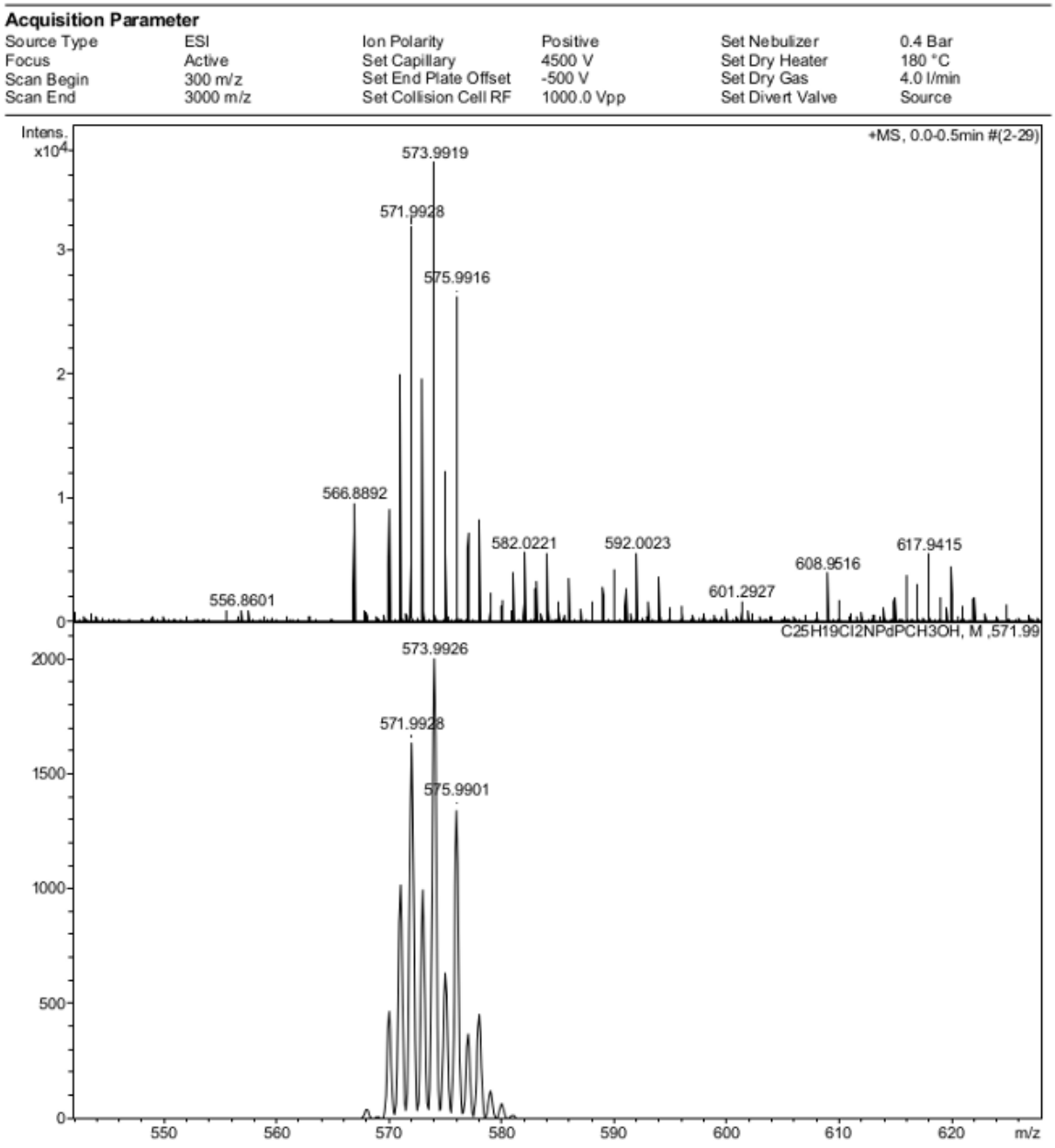


Figure S15. The fragment of mass-spectrum of **4** (top) and calculated isotopic distribution for ion $[M - Cl + CH_3OH]^+$ (bottom).

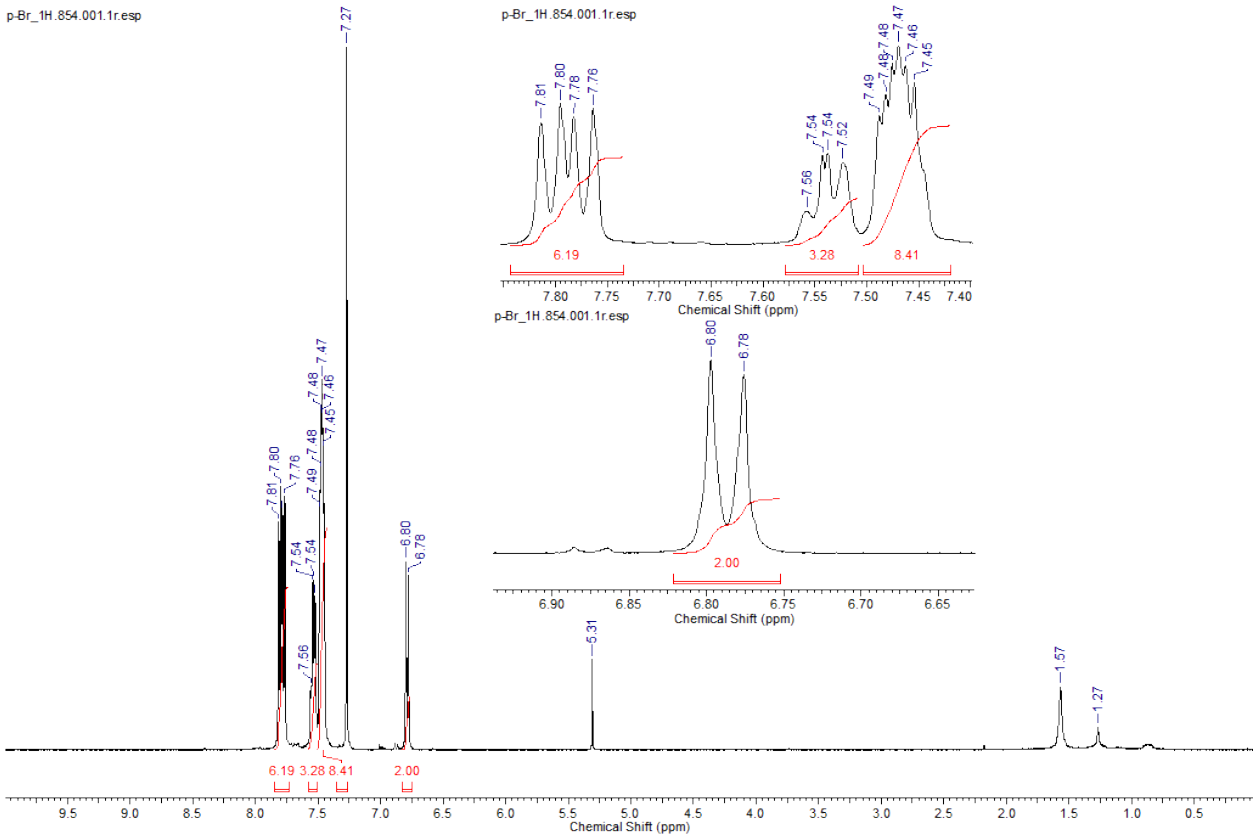


Figure S16. ^{1}H NMR spectrum of **5** ($CDCl_3$).

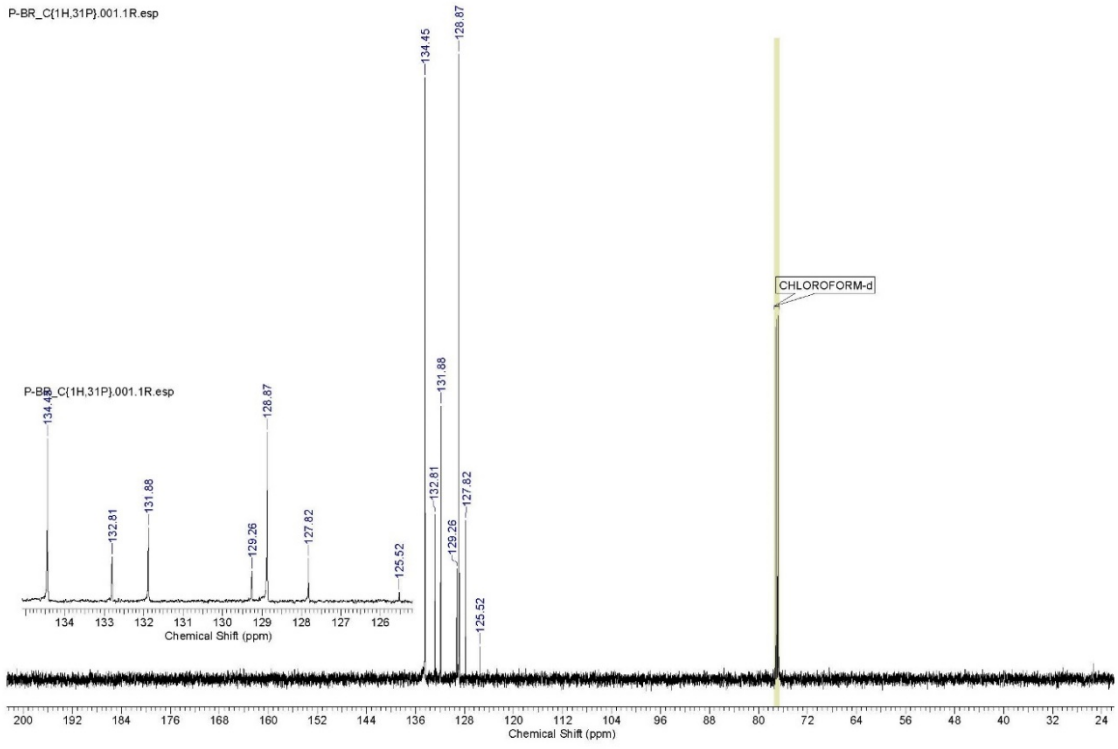


Figure S17. $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of **5** ($CDCl_3$).

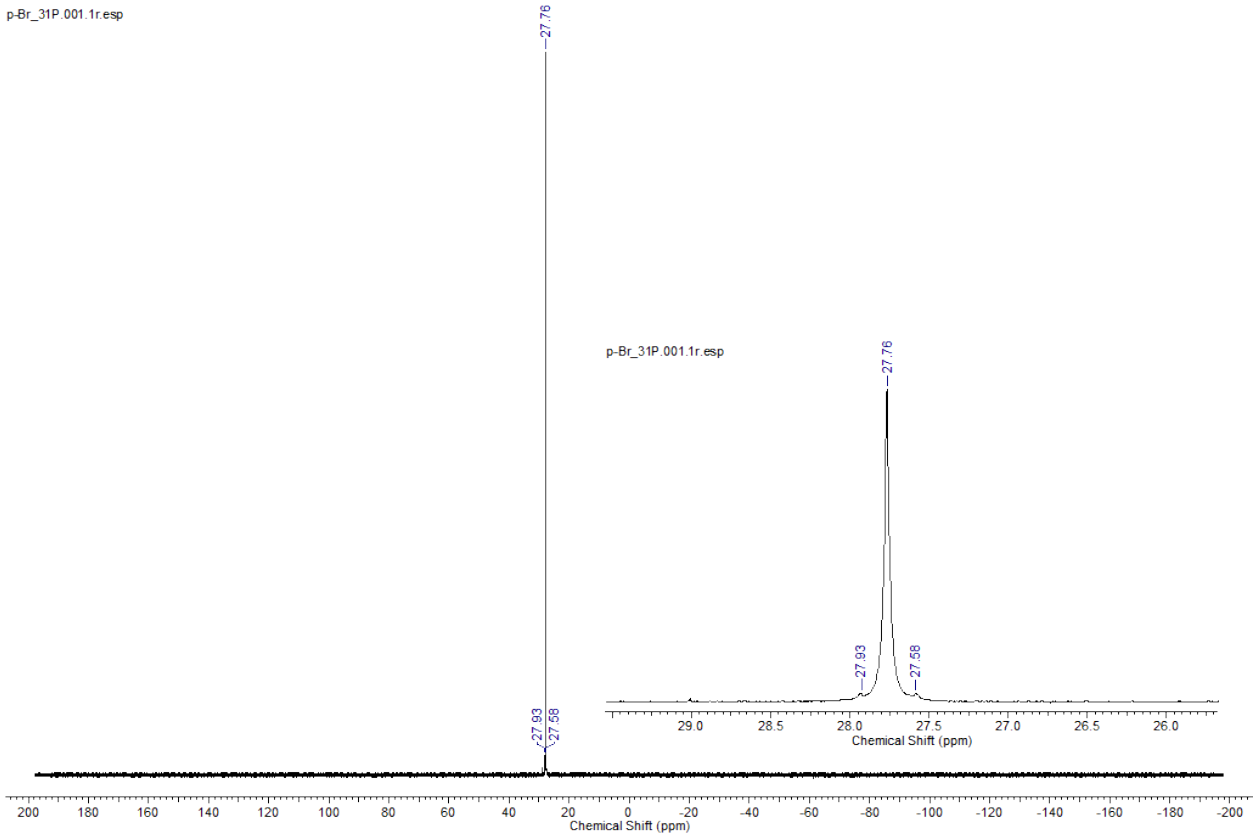


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$).

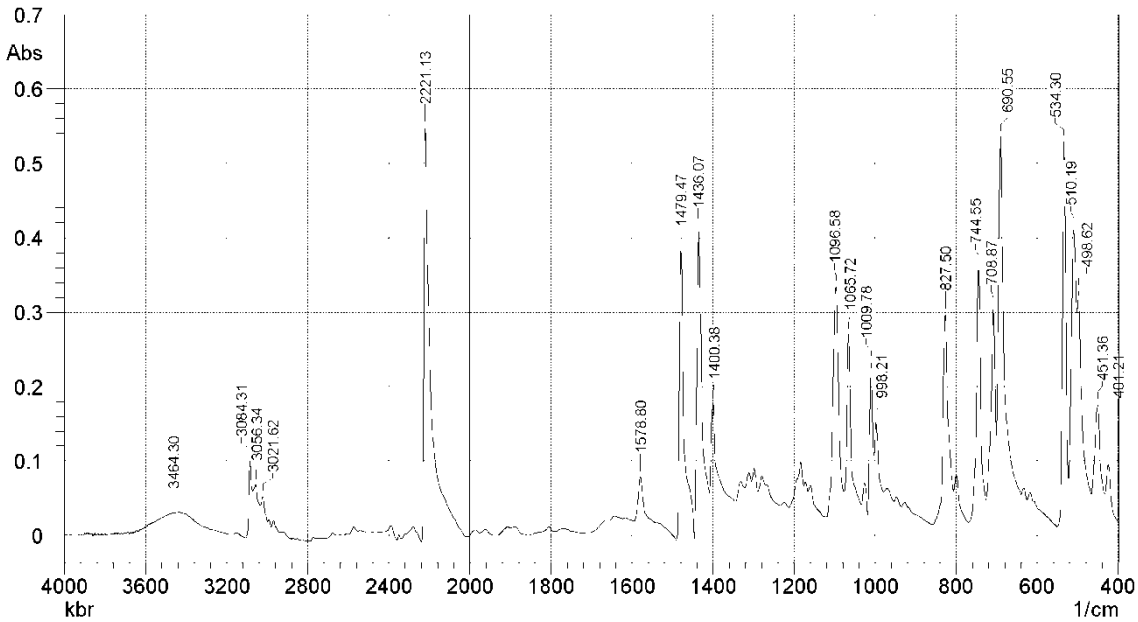


Figure S19. IR spectrum of **5** (KBr).

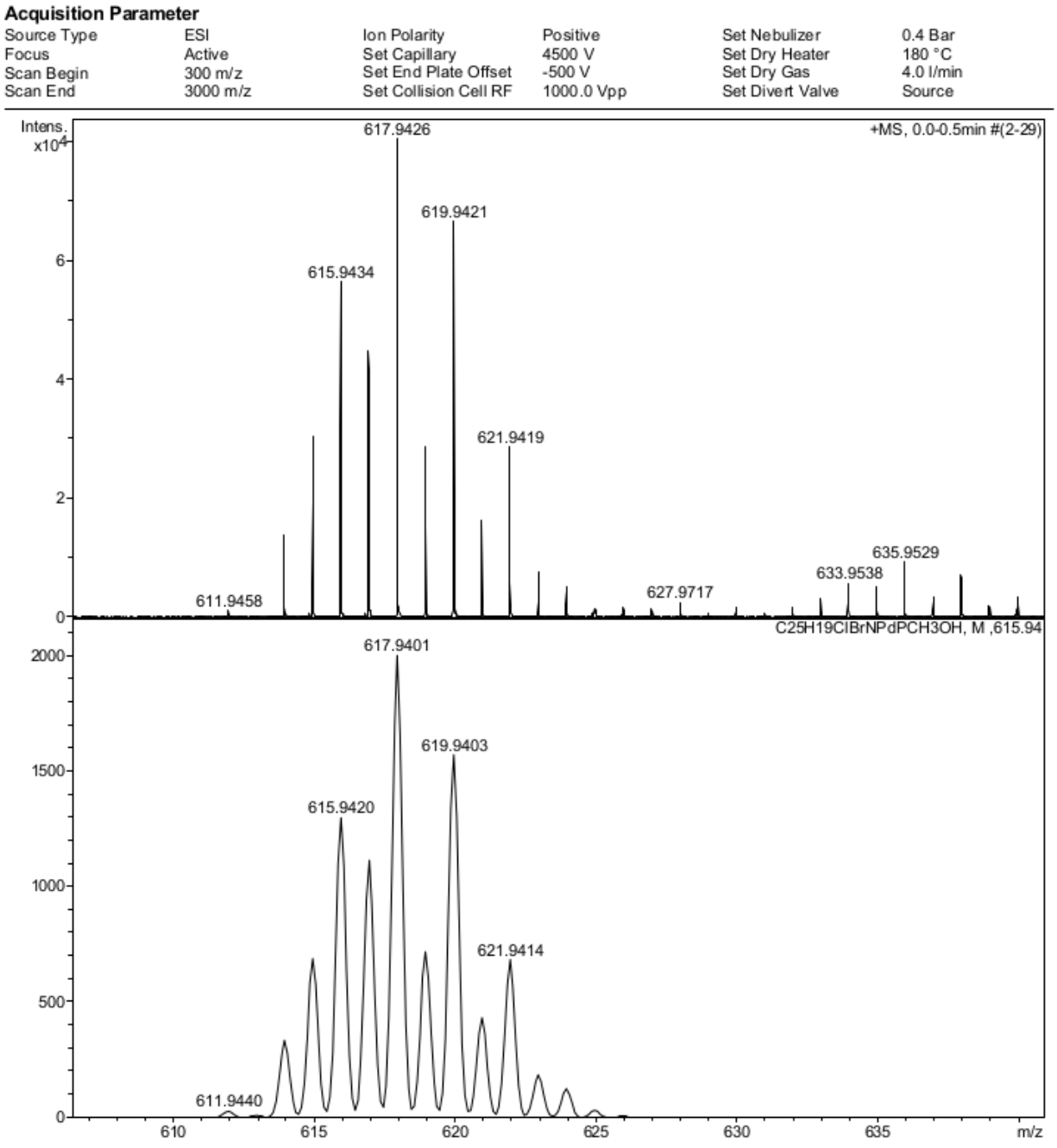


Figure S20. The fragment of mass-spectrum of **5** (top) and calculated isotopic distribution for ion $[M - Cl + CH_3OH]^+$ (bottom).

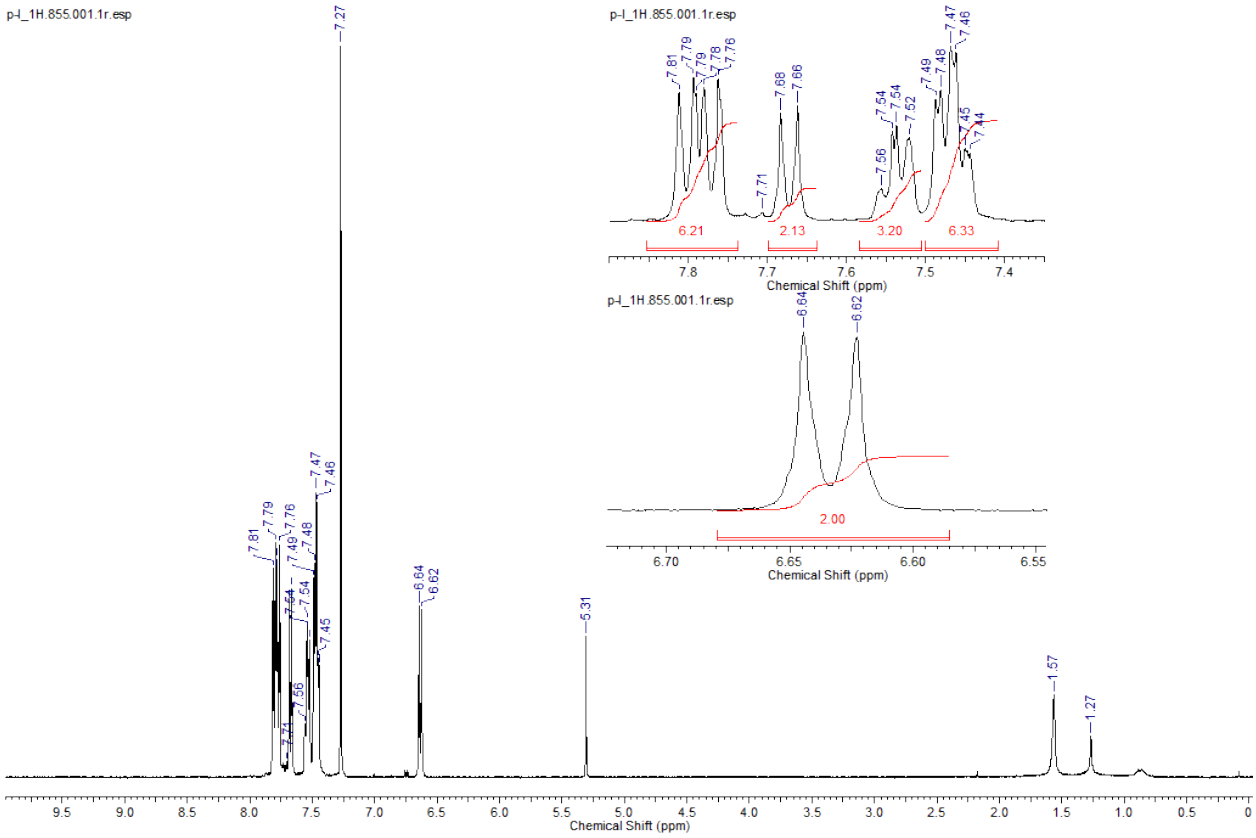


Figure S21. ^{1}H NMR spectrum of **6** ($CDCl_3$).

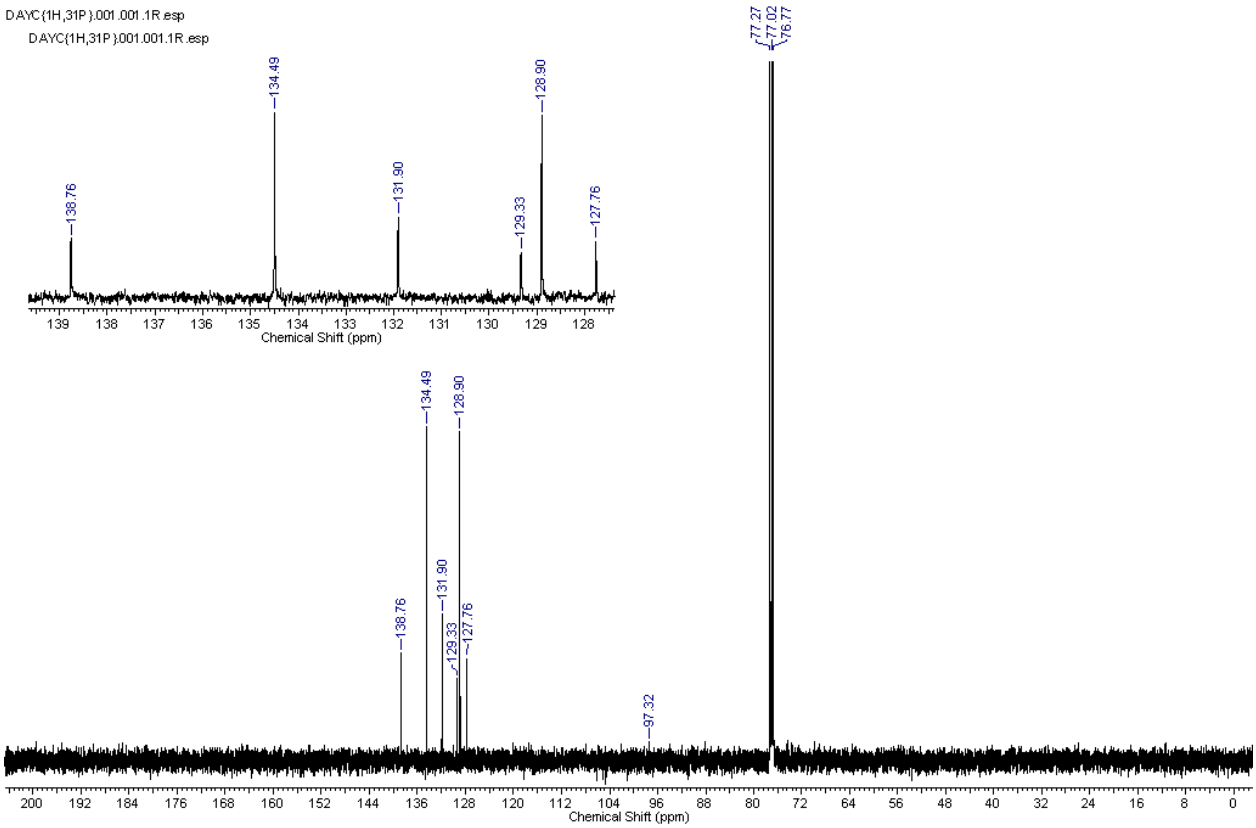


Figure S22. $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of **6** ($CDCl_3$).

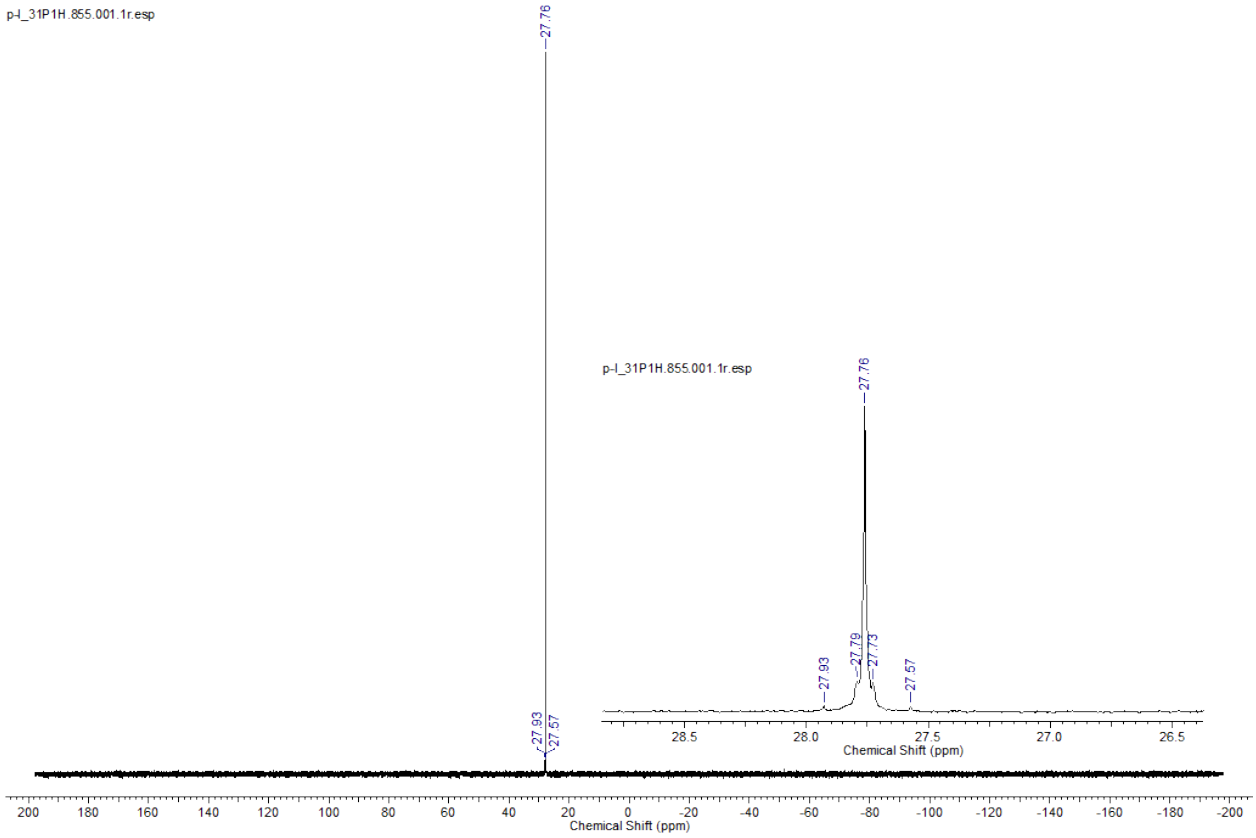


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$).

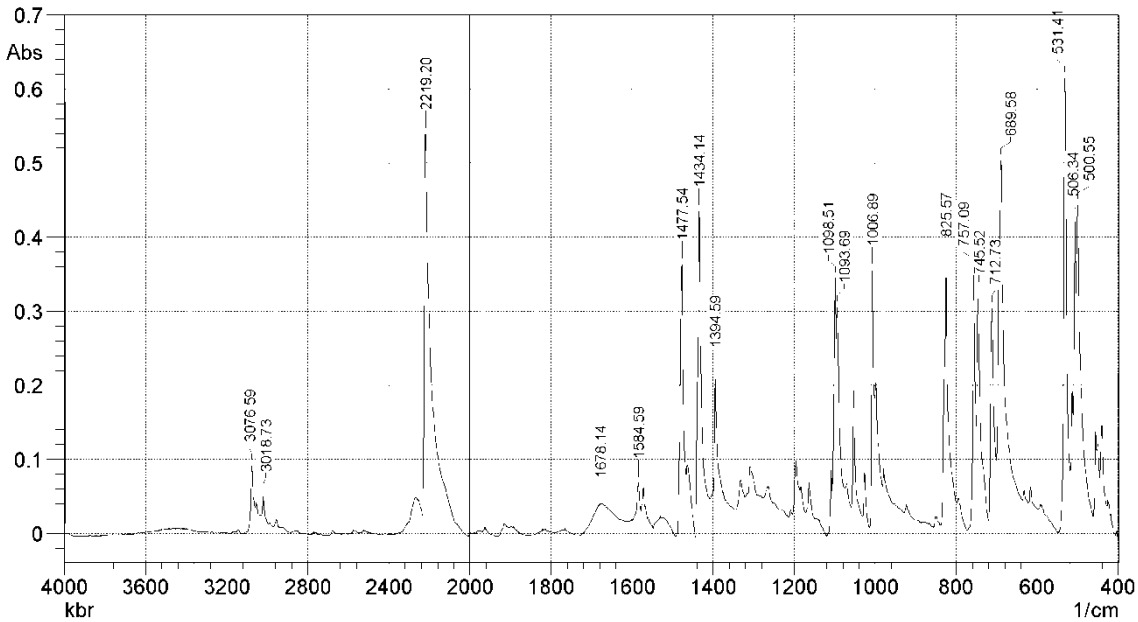


Figure S24. IR spectrum of **6** (KBr).

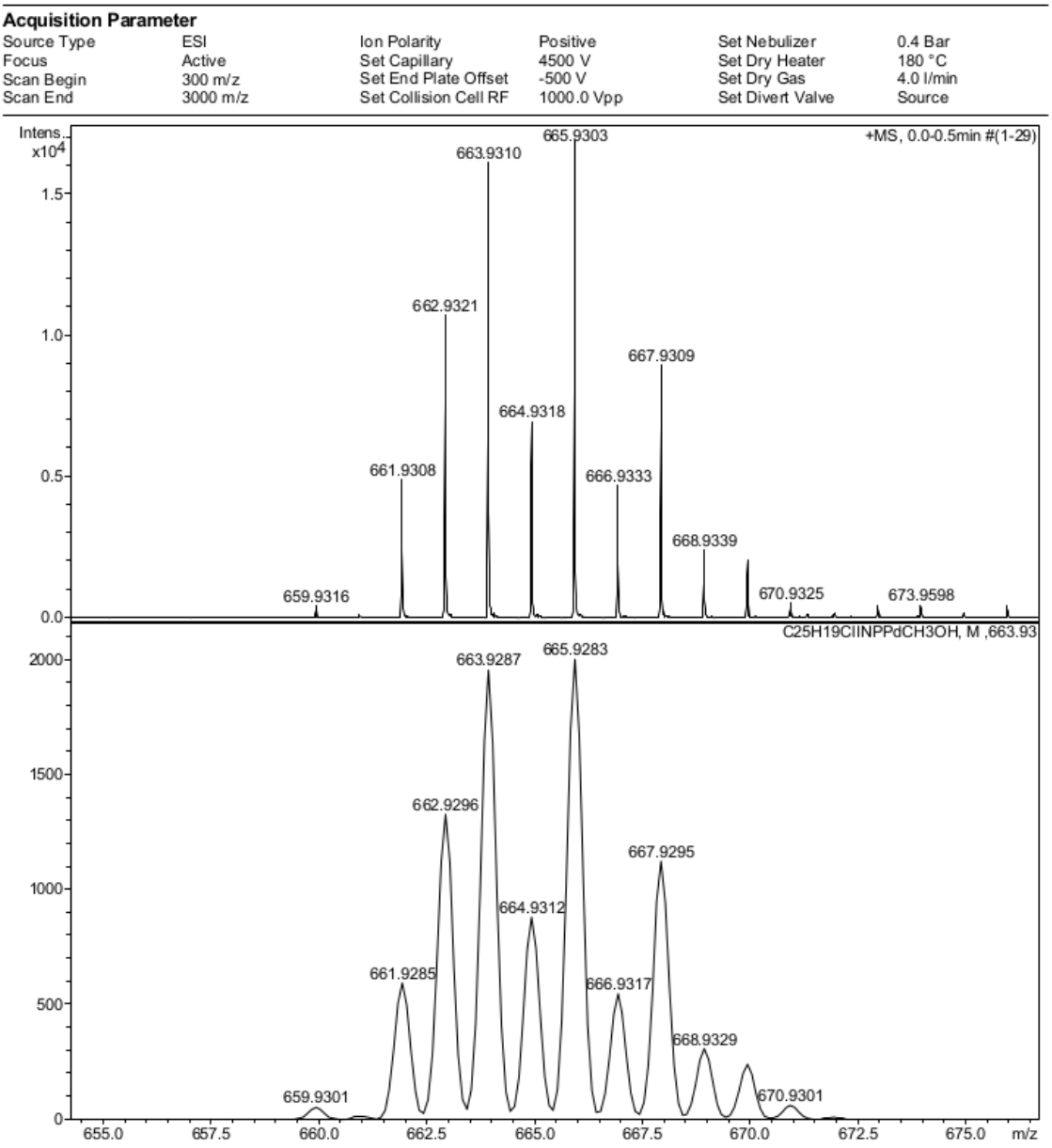


Figure S25. The fragment of mass-spectrum of **6** (top) and calculated isotopic distribution for ion $[M - Cl + CH_3OH]^+$ (bottom).

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